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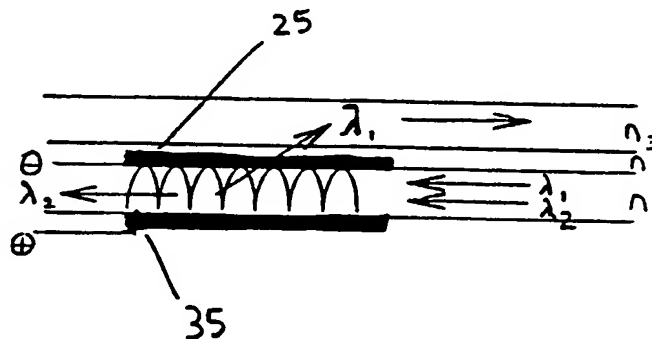
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(54) Title: A MULTI-FUNCTIONAL OPTICAL SWITCH (OPTICAL WAVELENGTH DIVISION MULTIPLEXER/DEMULTIPLEXER, ADD-DROP MULTIPLEXER AND INTER-CONNECT DEVICE) AND ITS METHOD OF MANUFACTURE



(57) Abstract: The invention provides a multifunctional optical switch that among other things, optionally can function as an optical wavelength division multiplexer, wavelength division demultiplexer, add-drop multiplexer and/or inter-connect device. The invention further provides novel methods of manufacturing the optical switch. The optical switch can comprise a single layer, and optimally includes of a plurality of layers which each comprise an optical nonlinear second-order polymer. The optical nonlinear second-order polymer present in each layer differs from that present in any other layer in terms of its absorption maximum (i.e., due to possession of different chromophores).

**A Multi-Functional Optical Switch (Optical Wavelength Division
Multiplexer/Demultiplexer, Add-Drop Multiplexer
and Inter-Connect Device) And Its Method of Manufacture**

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GOVERNMENT RIGHTS IN THE INVENTION

The invention was made with Government support under Agreement No. DASG60-98-M0158, awarded by the Ballistic Missile Defense Organization, U.S. Department of Defense. Accordingly, the government may have certain rights in the invention.

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TECHNICAL FIELD OF THE INVENTION

The present invention pertains to a multifunctional optical switch that can be employed *inter alia* as an optical wavelength division multiplexer, optical wavelength division demultiplexer, optical add-drop multiplexer and/or optical inter-connect device. The invention further provides novel methods of manufacturing the optical switch. The optical switch can comprise a single layer, and optimally includes a plurality of layers which each comprise an optical nonlinear second-order polymer. The optical nonlinear second-order polymer present in each layer preferably differs from that present in any other layer in terms of its absorption maximum (i.e., due to possession of different chromophores).

20

BACKGROUND OF THE INVENTION

The new century heralds an unprecedented demand for ability to transport and process large amounts of information. The incredible growth in demand for Internet resources and the constraints of bandwidth are but just two of the factors that compel the telecommunications industry to pursue less expensive and more efficient options in the form of "all-optical" networks (as well as networks that may not solely comprise, but do include, optical components).

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For industries to meet such demand, further development and improvement of optoelectronic components (currently bulky and expensive) is necessary. In particular, it will be necessary to: (i) reduce the size of the optical components; (ii) increase the number of channels on a given optical fiber; and (iii) simplify the fabrication process

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to reduce costs. In addition, higher and higher transmission bit-rates of data are needed to expand the capability of current fiber communication channels.

Wavelength division multiplexers (WDMs) have become one of the hottest commodity items in lightwave applications today since they allow multiple
5 wavelengths to be used as channels to transmit data within a single optical fiber. WDMs traditionally are based on inorganic materials. However, organic materials, namely polymeric materials, have recently reached a performance maturity to compete with these inorganic optical materials. Such materials exhibit physical and chemical
10 "flexibility", and, for instance, can be relatively easily chemically modified to suit specific applications. This flexibility of polymeric materials makes possible, among other things, rapid cycles of material design, preparation, testing, and redesign. Organic polymeric materials are readily fabricated into integrated optical circuitry, which contributes to lower costs of manufacture. Polymer-based devices could
15 ultimately be mass-produced using simple printing processes. Moreover, organic polymers provide a large inventory of photonic materials that can have a low dielectric constant. Certain of the polymers show high stability and optical nonlinearity.

In the 1990s, polymer-based interferometers and other polymer-based devices generated great interest (Girton et al. "Electrooptic Polymer Mach-Zehnder Modulator." *In* ACS Symposium Series 601, *Polymers for Second-Order Nonlinear*
20 *Optics* (Washington D.C. 1995), 456-468). Polymeric materials have recently emerged as materials for use in optical applications (Keil, "Realization of IO-Polymer-Components and present State in Polymer Technology" *In Integrated Optics and Micro-Optics With Polymers*, (Stuttgart-Leipzig: B.G. Teubner Verlagsgesellschaft, 1993), 273; Ito et al., eds., *Polymeric Materials for*
25 *Microelectronics Applications*, ACS Symposium Series 579 (Washington, DC: American Chemical Society, 1991); Lindsay et al., eds., *Polymers for Second Order Nonlinear Optics*, ACS Symposium Series 601 (Wash., DC: American Chemical Society, 1995), pp. 1, 111, 130, 158, 172, 374, 381; Edelman et al., eds.

Among the more recently developed polymeric materials are polyimides that
30 have been shown to have superior optical and physical characteristics. In particular, certain polyimides show thermal stability, as well as high optical nonlinearity (as reflected in their r_{33} values) (Lindsay et al., *supra*). The company Akzo Nobel uses polymers to make optical switches. Similarly, the company Lightwave has combined

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optical design with a polymer-materials technology and semiconductor techniques to make waveguide structures directly on a wafer where the silicon acts as a platform only. Lightwave uses a polyimide polymer having a low dielectric constant and high temperature stability and uses heat to change the refractive index (i.e., the polymers
5 are thermo-optic polymers). The material made by Lightwave acts as an optical pipe, and theoretically could be made optically active by applying a voltage across the material to change the index of refraction. Then the light can be modulated or switched from one path to another, or just modulated at high speeds. Despite these advances, considerable advances in the optics field still need to be made to meet the
10 recent demands of the telecommunications industry. For instance, devices constructed to date are single-layer devices, and/or are planar (i.e., the switching occurs in one plane to adjacent waveguides).

Thus, the present invention provides a novel device, i.e., an optical switch, that can perform several critical tasks for the telecommunications industry – e.g.,
15 wavelength division multiplexing, wavelength division demultiplexing, performance as an add/drop filter and/or interconnect device. The present invention further provides an optical waveguide. The switches and waveguide according to the invention conceivably can be manufactured more easily and at less than the cost of the silicon-based devices due to novel means for their production, as further described
20 herein. These and other objects and advantages of the present invention, as well as additional inventive features, will be apparent from the following description of the invention provided herein.

BRIEF SUMMARY OF THE INVENTION

25 The present invention pertains to a multifunctional optical switch, and novel methods for its manufacture. The optical switch can comprise a single layer, and optimally comprises a plurality of layers (i.e., at least two layers, preferably which are stacked), which desirably each comprise an optical nonlinear second-order polymer. The optical nonlinear second-order polymer present in each layer preferably differs
30 from that present in any other layer in terms of its light absorption maximum. The optical switch according to the invention desirably can be employed as an optical wavelength division multiplexer, wavelength division demultiplexer, add-drop multiplexer and/or inter-connect device, among other things. Other uses of and

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devices according to the optical switch (and the optical waveguide) of the invention would be apparent to one skilled in the art.

BRIEF DESCRIPTION OF THE FIGURES

5 **Figure 1** depicts the chemical structure of polyimide-alkoxy sulfone diazo.
Symbol: n, ranging from about 20 to about 600.

Figure 2 depicts the chemical structure of polyimide-dialkyl amino nitro azo.
Symbol: n, ranging from about 20 to about 600.

Figure 3 depicts the chemical structure of polyimide-dialkyl amino nitro
10 diazo. *Symbol:* n, ranging from about 20 to about 600.

Figure 4 shows the absorption spectra in terms of arbitrary absorbance units (0 to 1.8) at an applied wavelength (250 to 800 nm) of three second-order nonlinear optical polyimides having different pendant chromophores – i.e., sulfone diazo (Mordant Orange 10) chromophore present in a polyimide or poly(methyl
15 methacrylate) host matrix (“A” peak), dialkyl amino nitro azo present in polyimide-dialkyl amino nitro azo (“B” peak), and dialkyl amino nitro diazo present in polyimide-dialkyl amino nitro diazo (“C” peak). For this figure, three different absorbences are superimposed. The absorbances are obtained from different thickness films and do not correspond to scale.

20 **Figure 5** depicts the chemical structure of polyamic acid doped with a sulfone-diazo chromophore. *Symbol:* n, ranging from about 20 to about 600.

Figure 6 is a diagram of a buffered waveguide and the corresponding differing refractive indices n_1 , n_2 , and n_3 , that define each layer.

Figure 7 is a diagram showing a preferred apparatus to be employed for
25 waveguide fabrication by a direct laser writing technique. *Symbol:* 10, sample; 20, X-Y stage; 30, optical table; 40, nitrogen hood; 50, corona discharge; 60, high voltage supply; 70, laser; 80, laser beam; 90, lens; 100, mirror; 110, beam monitor; 120, computer.

Figure 8 depicts chromophore alignment of polyimide-dialkyl amino nitro
30 diazo, which is measured by in situ second harmonic generation (SHG; arbitrary units from 0 to 2.0) at room temperature over the course of 2000 seconds, with the onset (“Corona ON”) and termination (“Corona OFF”) of corona discharge depicted.

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Figure 9 is a diagram showing another preferred apparatus to be employed for waveguide fabrication by a direct laser writing technique. *Symbol:* 10, sample; 20, X-Y stage; 30, optical table; 70, laser; 80, laser beam; 85, half wave plate; 90, lens; 100, mirror; 110, beam monitor; 120, computer.

Figure 10 depicts holographic grating formation using two overlapping laser beams which intersect at an angle α in the polymeric waveguide material. The relationship between angle of incidence in the laser beams (α) and other geometrical parameters can be solved geometrically according to Figure 10, where h is the distance between the beam splitter (130) and the sample (140), b is the distance between the mirror (100) and the beam splitter (130) and β is the angle between b and h as shown in Figure 10. *Symbols:* 80, laser beam; 100, mirror; 130, beam splitter; 140, polymeric material.

Figure 11 shows photobleaching steps for waveguide fabrication and subsequent grating formation with use of laser beams. *Symbols:* 80, laser beam; 140, polymeric material; 150 metallic (e.g., quartz) mask; 160, irradiation; 170, unbleached waveguide; 180, bleached polymeric material; 190, grating formation.

Figure 12 shows parameters for single mode guiding in a rib waveguide where "h", "w", and "t" are, respectively, the height of the non-bleached portion of the polymer layer, the width of the non-bleached portion of the polymer layer, and the height of the bleached portion of the polymer layer. *Symbols:* 140, polymeric material; 170, unbleached waveguide; 180, bleached polymeric material; 250, solid support.

Figure 13 diagrams a passive three-layer multiplexer that consists of two waveguides connected by a holographically bleached or "surface relief" grating. *Symbol:* n_1 and n_2 are the refractive indices of separate 2^o-NLO polymers present on independent waveguides; n_2 is the refractive index of buffer; spiral, Braggs-Grating; λ_1 and λ_2 , wavelengths. The direction of light propagation of λ_1 in layer n_3 is dependent on the spacing (or pitch) of the grating in n_2 .

Figure 14 diagrams an active three-layer device where n_1 , and n_3 are the refractive indices of different second-order nonlinear optical polymers (e.g., polyimide-alkoxy sulfone diazo (Mordant Orange 10), polyimide-dialkyl amino nitro azo, and/or polyimide-dialkyl amino nitro diazo), n_2 is the refractive index of the

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buffer layer, and the refractive index can be changed by applying an electric field across the waveguide. *Symbols:* 25, top electrode (preferably transparent such as an ITO electrode or a very thin metal); 35, bottom electrode; λ_1 and λ_2 , wavelengths; spiral, Bragg-Grating; +/-, applied electric field. The direction of light propagation of λ_1 in layer n_3 is dependent on the grating spacing and the applied voltage in n_1 .

Figure 15 diagrams a double grating "resonance matched" multiplexer, where n_1 and n_3 are the refractive indices of different second-order nonlinear optical polymers present in the layers (e.g., polyimide-alkoxy sulfone diazo (mordant Orange 10), polyimide-dialkyl amino nitro azo, and/or polyimide-dialkyl amino nitro diazo) and n_2 is the refractive index of a buffer layer. *Symbols:* 25, top electrode preferably transparent such as an ITO electrode, or a very thin metal); 35, bottom electrode λ_1 and λ_2 , wavelengths; spiral, Bragg-Grating; +/-, applied electric field. The direction of light propagation of λ_1 in layer n_3 is dependent on the position of the grating in n_1 , the spacing of grating in n_1 and n_3 and the applied voltage in n_1 .

Figures 16A-B show an illustrative embodiment of the basic device configuration shown schematically in **Figure 11**. With the top view depicted in **Figure 16A**, and the side view depicted in **Figure 16B**. *Symbols:* 25, top electrode preferably transparent such as an ITO electrode, or a very thin metal); 35, bottom electrode λ_1 and λ_2 , wavelengths; spiral, Bragg-Grating; +/-, applied electric field; 250, solid support. The direction of light propagation of λ_1 in layer n_3 is dependent on the spacing of the grating and applied voltage in n_1 .

Figure 17 depicts a sample 4 x 4 multiplexer/demultiplexer and cross-connect device according to the invention. *Symbols:* 200, enclosure box; 210, optical circuit board; 220, electrical connections; 230, input optical fibers; 240, output optical fibers.

25

DETAILED DESCRIPTION OF THE INVENTION

The invention pertains to a multifunctional optical switch that, among other things, desirably can function as an optical wavelength division multiplexer, optical wavelength division demultiplexer, optical add-drop multiplexer and/or optical inter-connect device. In particular, the invention pertains to an optical device, particularly an optical frequency dispersive device, such as an optical multiplexer or optical demultiplexer, which preferably receives light from one or more input waveguides and

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disperses it according to frequency to one or more output waveguides. The present invention also optimally pertains to an optical add/drop multiplexer and to an inter-connect device.

According to the invention, preferably a "device" includes any single preferred entity as set forth herein (e.g., including, in particular, a waveguide), or any combination of elements (e.g., optical switch, optical wavelength division multiplexer, optical wavelength division demultiplexer, optical add-drop multiplexer, optical inter-connect device and the like) either alone, or, in a higher level of organization (e.g., present in a system or subsystem such as a board or motherboard). Preferably these entities are employed in optical communication systems, although each may exist in any combination, or independently, or as part of a communications system or other system that is other than predominantly optical (i.e., a mix of optical and nonoptical systems). Desirably a device according to the invention is optically active (as further described herein), although passive devices are also contemplated by and preferred according to the invention. However, one unifying feature of all the elements of the invention is their incorporation of a second-order nonlinear optical (2°-NLO) polymer, or a polymer having the desirable properties set forth herein, as further described below.

Certain standard terms are employed in describing the invention. Illustrative definitions of these terms are set out below, and in the Examples which follow. Should there be any term that is left undefined, or any possible ambiguity in the meaning of a term, the broadest possible definition known in the optics/electronics fields that is consistent with the scope and goals of the invention is to be applied. Also, like numbering is used for the same components in each of the Figures and in the descriptive text.

The expression "optical communication system" or "optical system" as used herein refers to any system which employs optical signals to convey information across an optical waveguide medium. Such optical systems include, but are not limited to, telecommunications systems, cable television systems, local area networks (LANs), and the like.

A "waveguide" is an entity of material boundaries or structures for guiding electromagnetic waves. More specifically, a waveguide is an optical waveguide, or

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any structure capable of guiding optical power (i.e., carrying one or more optical signals).

A "second-order nonlinear optical" (2°-NLO) polymer is a polymer that is optically active -- i.e., its index of refraction changes due to an applied electric field, and the change is proportional to the square of the applied electric field. Preferably according to the invention, a 2°-NLO polymer is obtained by the incorporation into a polymer backbone of a chromophore having 2°-NLO characteristics, and/or which exhibits those characteristics when present in the polymer backbone.

According to the invention, a waveguide preferably is comprised of a layer of 2°-NLO polymer. Desirably the waveguide is flanked on at least one side by a solid support capable of supporting the waveguide, wherein the solid support can be any appropriate material, e.g., glass, plastic, metal, and the like. The solid support need not be entirely rigid (although completely rigid materials can be employed), but can have some amount of flexibility. Preferably the waveguide also is flanked on at least one side by cladding. Whenever a solid support is employed to support the waveguide, the support must not directly contact the waveguide, but must be separated from the waveguide by cladding. It is necessary for proper functioning of the waveguide that the index of refraction in any layer that directly contacts the waveguide (i.e., on one or more sides, and preferably on all sides) is less than the index of refraction in the waveguide itself. Accordingly, cladding can include one or more layers of any appropriate material that has an index of refraction that is less than the index of refraction in the waveguide itself, such as 2°-NLO polymer, glass, plastic, silica, or other appropriate material, and further can include a buffer (e.g., as set out in Figure 6, and in other figures). According to the invention, "a buffer" is an optical buffer, i.e., a medium that does not exhibit any optical activity or optical nonlinearity with lower refractive index. Optionally according to the invention, the cladding layers can be conductive as described in U.S. Patent 5,887,116 (incorporated by reference).

The index of refraction in each layer (e.g., of a waveguide or of an optical switch) is impacted by the chromophore concentration, the nature of the chromophore, and the nature of the polymer backbone. Of course, these parameters can easily be optimized by one skilled in the art. Desirably, the waveguide can comprise any part of a circuit or optical device (i.e., an optical switch).

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As indicated previously, to function as a waveguide, the index of refraction in any layer surrounding the waveguide must be less than the index of refraction in the waveguide itself. This difference in refractive index between the waveguide itself and any adjacent layer (i.e., " Δn " in Example 2) preferably is equal to or greater than 0.001, and desirably is no more than 0.1. However, with alternate thicknesses of waveguide, it is conceivable that the range of differences may be slightly broader. Such alternates are contemplated by the present invention.

Thus, desirably the present invention contemplates an "asymmetric waveguide" and a "symmetric waveguide". In the case of an asymmetric waveguide, i.e., comprised of a waveguide surrounded by an upper and lower cladding layer, the refractive indices of the upper and lower layers are not equal to each other, and are less than the refractive index of the waveguide. In the case of a symmetric waveguide, i.e., comprised of a waveguide surrounded by an upper and lower cladding layer, the refractive indices of the upper and lower layers are equal to each other, and are less than the refractive index of the waveguide. This is further described in Example 2.

An "optical switch" is a device that is capable of changing the path of light from one waveguide to another (e.g., a multiplexer/demultiplexer, add/drop multiplexer, and/or interconnect), or from one waveguide to air or cladding (e.g., as a drop multiplexer, and/or connected to a detection device).

An "optical multiplexer" is a device which combines a plurality of optical signals having different wavelengths in a single optical fiber on the transmitting side. An "optical demultiplexer" is a device which separates a multiplexed signal into a plurality of optical signals of different wavelengths on the receiving side. Essentially, an optical multiplexer is an optical demultiplexer run in reverse, and vice versa.

In particular, an optical "wavelength division multiplexer" ("WDM") is a system that employs WDM signals consisting of a number of different wavelength optical signals (known as "carrier signals" or "channels") to transmit information on optical fiber or in an optical waveguide. In a WDM system, optical signal channels are generated, multiplexed (i.e., added together) to form an optical signal comprised of the individual optical signal channels, transmitted over a single waveguide, and demultiplexed (i.e., separated) such that each channel wavelength is individually routed to a designated receiver. The various channels within a WDM signal can be

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distinguished by their optical wavelength and/or their optical frequency, with these terms being used interchangeably herein as features of the optical signal.

An optical "add/drop multiplexer" (OADM) is a device which facilitates the addition (i.e., add multiplexing) and/or subtraction (i.e., drop multiplexing) of particular carrier signals to or from the WDM signal at different locations on an optical network. For instance, such routing can occur when optical channels are sent to or withdrawn from an optical transmission line, e.g., for sending optical channels between a terminal and an optical bus, or for routing long distance telecommunications traffic to individual cities, or for other uses. An OADM is thus essentially just a variation of a WDM such as is known in the art.

An "optical interconnect" (OIC) or "optical cross-connect" (OXC) provides routing of signal at the optical (wavelength) level. An OIC/OXC can route a signal from point A to point B or C. It provides wavelength management on a number of incoming and outgoing fibers, and optimally can contribute to optical grooming and restoration capabilities.

An "active" device according to the invention is one which responds to an applied electric field. An active device must contain at least one grating, but each waveguide present in the device (i.e., in the case of a device comprised of more than one waveguide) need not necessarily contain a grating. In other words, with an active device, its optical properties are changed when a voltage is applied to it. By comparison, a "passive" device according to the invention is one that does not change its characteristics when a voltage is applied to it, and/or a device that functions without needing to apply a voltage (i.e., and to which a voltage is not applied).

According to the invention, the electric field is generated with any appropriate power source (e.g., AC or DC power source), and communicated to the device or switch by means of an electrode. The electrode used in the present invention preferably is made of at least one of the following materials: metals such as gold, silver, platinum, copper, and alloys; conductive materials such carbon black, conductive epoxy, or indium tin oxide (ITO). However, any electrode having the ability to conduct charge and capable of functioning as an "electrode" as that term is understood in the art can be employed in the methods and devices of the invention. Generally, an electrode need only supply a small amount of voltage, e.g., from 0 to

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about 50 volts, although in certain applications, it may be preferable to employ a higher voltage.

According to this invention, a "grating" is a means of separating an optical signal. A particularly preferred grating for use in the invention is a Bragg-Grating. A "Bragg-Grating" is an element for selectively controlling specific wavelengths of light within a waveguide. A typical Bragg-Grating contains a length of waveguide that includes a plurality of periodic perturbations in the index of refraction, wherein the perturbations are substantially equally spaced along the length of the waveguide. These perturbations selectively reflect light having a wavelength (λ) equivalent to twice the spacing (Λ) between the successive perturbations (i.e., $\lambda = 2n_{eff}\Lambda$, where λ is the vacuum wavelength and n_{eff} is the effective refractive index of the propagating mode). The light that is not selectively reflected by the Bragg-Grating passes through the grating unimpeded.

Conventional gratings such as the Fiber Bragg-Grating are typically manufactured by using a waveguide (e.g., an optical fiber) that includes one or more elements in their core that are sensitive to ultraviolet light, and then exposing the waveguide at periodic intervals to high intensity ultraviolet light (or other appropriate light), e.g., from an excimer laser. Generally, the appropriate periodic spacing of perturbations in a grating is accomplished with use of some sort of physical mask to adjust areas exposed to the laser (e.g., a photo mask), a phase mask, or a pair of interfering beams (e.g., holographic techniques). Further preferred approaches for generation of a grating according to the invention, particularly a Bragg-Grating, are described below, and in the Examples which follow, as well as are illustrated in Figure 10. However, other means of grating generation known in the art optionally can be employed.

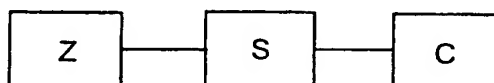
In particular, preferably the present invention provides an active Bragg-Grating multiplexer (desirably produced via optical waveguide writing techniques such as photobleaching and laser writing as further described herein), in thin layers fabricated from soluble, second-order nonlinear optical (2°-NLO) polymers. The invention further provides a demultiplexer, OADM, an OIC/OXC, and other active and passive devices. Preferably such devices according to the invention comprise a single layer of 2°-NLO, and optimally comprise more than one layer of the 2°-NLO, especially from

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two to ten layers of different 2°-NLOs, desirably from two to six layers of different 2°-NLOs, and particularly two or three layers of different 2°-NLOs. When more than a single layer of 2°-NLO is present, optimally according to the invention the layers are “stacked” (although a side-by-side juxtaposition also can be employed). Desirably the optical switch devices as described above further comprise one or more buffer layers, as well as other optional components (e.g., interferometer). Preferably, the grating(s) (e.g., Bragg-Grating(s)) are present in the buffer layer(s) and/or the waveguide layer(s) comprised of 2°-NLOs.

Preferably the 2°-NLOs employed in the invention (or other appropriate polymer) exhibit thermal and mechanical stability, and high optical non-linearity. Desirably the 2°-NLO does not suffer thermal decomposition until above about 300°C. Optimally the 2°-NLO has a large electro-optic coefficient (r_{33}) ranging anywhere from between about 5 to about 40 picometer/volt (e.g., as reported in the literature).

It particularly is preferred according to the invention that the 2°-NLO is a polyimide, i.e., having as a “polymer backbone” poly [N, N (1,4 phenylene)-4, 4’ (hexa fluoroisopropylidene) diphthalic imide] depicted as “Z” in Structure I below and hereafter referred to generally as “polyimide” (although “S” and “C” present in the polyimide may differ, and are further described below):



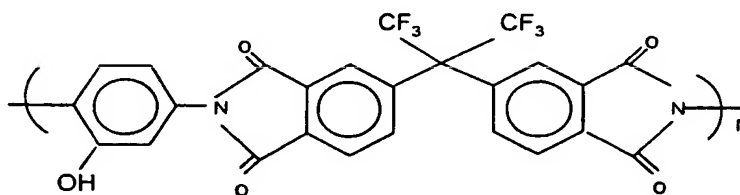
Structure I

In Structure I, the preferred structure of the 2°-NLO polymer according to the invention, the polymer backbone is attached to a spacer, “S”, which itself is attached to a chromophore “C”, each of which is further described below. The polyimide according to the invention optionally can be modified or substituted if beneficial for a particular application, so long as such modification/substitution allows functionality within the spirit and scope of the invention. Alternately, instead of the chromophore being covalently attached to the polymer backbone, the chromophore desirably can be non-attached and used to dope the polymer.

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In situations where it is not necessary that the polymer backbone exhibit thermal stability above 300°C, the polymer backbone can comprise the following polymers (or other polymers) instead of polyimide, and which have the thermal glass transition values (°C) indicated: Poly(methyl methacrylate), 114; Polystyrene, 100; Poly(p-hydroxystyrene), 150; Polycarbonate, 150; Polyester, 38-130; Polyurethane, 140; Poly(phenylene vinylene), 40; Polyquinoline, 175; Polyamide, 276; Polyimide, 310. Thus, desirably according to the invention, these other polymers can be employed instead of polyimide as the polymer backbone "Z".

In particular, however, preferably the polymer backbone "Z" is polyimide, i.e., having Structure II (M_w of about 454) depicted below:



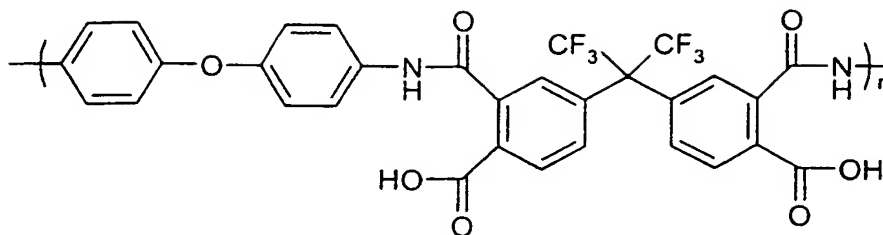
Structure II

where n preferably is any number ranging from about 20 to about 600, and desirably ranges from about 100 to about 300. Generally it is found that longer chains (i.e., where n is greater than 20) give better properties in the sense that the chains intertangle better. Too great of a chain length, however, deleteriously impacts polymer solubility.

It further is desirable according to the invention that the polymer backbone "Z" is a polyamic acid having Structure III depicted below, and which upon heating becomes insoluble in organic solvents:

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Structure III

where n preferably is any number ranging from about 20 to about 600, and desirably
 5 ranges from about 100 to about 300.

The spacer, "S", in Structure I preferably is a chain of from 0 to 30 carbons (or
 other moieties, including attached moieties, such as hydrogen, and functional groups
 including but not limited to alkyl groups) which provides optimal spacing such that
 the polymer backbone is appropriately attached to, and does not interfere with, the
 10 functionality of the chromophore ("C"). In particular, preferably the spacer has a
 length of from 1 to 10 atoms, and even more desirably, from 2 to 6 atoms. However,
 the spacer must be of sufficient length and character such that it does not interfere
 with the function of (e.g., the conjugation of) the attached chromophore, as well as
 does not interfere with the 2°-NLO properties of the polymer. A preferred spacer
 15 according to the invention is oxytrimethylene spacer. Other preferred spacers are
 those depicted in Figures 1-3 (shown already attached to the polymer backbone).

With regard to the chromophore, "C," the 2°-NLOs polyimide with chemically
 attached (i.e., polyimide-alkoxy sulfone diazo) or doped sulfone diazo (Mordant
 Orange 10, purchased from Sigma-Aldrich Fine Chemicals, St. Louis, Missouri),
 20 chromophore, polyimide-dialkylamino nitro azo, and polyimide-dialkyl amino nitro
 diazo (see, Saaedeh et al., "Polyimides with a Diazo Chromophore Exhibiting High
 Thermal Stability and Large Electrooptic Coefficients", *Macromolecules*, 30 (18),
 5403-5407 (1997); Yu et al., "Novel Second-Order Nonlinear Optical, Aromatic and
 Aliphatic Polyimides Exhibiting High-Temperature Stability", *Applied Physics*
 25 *Letters*, 66, 1050-1052 (1995); Yu et al., "Novel Second-Order Nonlinear Optical
 Polyimides," *Society of Photooptical Instrumentation Engineers*, 2527, 127-136) are
 especially preferred for use in the invention. These polyimides incorporate the
 chromophores dialkyl amino nitro azo (e.g., present in polyimide-dialkyl amino nitro

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azo). sulfone diazo (e.g., present in polyimide-sulfone diazo). and dialkyl amino nitro diazo (e.g., present in polyimide-dialkyl amino nitro diazo). These polyimides (as well as other polyimides, or other polymers appropriate for optical applications) optimally can be modified by the incorporation of different chromophores into the polyimide backbone, allowing the responsiveness of the 2°-NLO to different wavelengths of light to differ.

Such modification of the polyimide backbone with different chromophores is known in the art, and is described, for instance, in Marder et al., *Nature*, 388, 845-851 (1997). The chromophore incorporated in the polyimide can be any chromophore, but desirably is a chromophore including, but not limited to: (a) the three chromophores previously described, and (b) those chromophores depicted in **Table 1**. In **Table I** below, " μ " is the dipolar moment of the molecule, " β " is the hyperpolarizability, and " λ " is the wavelength.

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Table 1

	Structure	$\mu\beta \times 10^{48}$ (esu)	λ_{\max} (nm)
1	 NMe_2 -C ₆ H ₄ -CH=CH- _n -C ₆ H ₄ -NO ₂ $n=2$ $n=3$ $n=4$	813 1074 1700	442 458 464
2	 Me_2N -C ₆ H ₄ -N=N-C ₆ H ₄ -NO ₂	751	480
3	 NPh_2N -C ₆ H ₄ -N=N-C ₆ H ₄ -NO ₂	788	486
4	 Et_2N -C ₆ H ₄ -N=N-C ₆ H ₄ -NO ₂	996	494
5	 NPh_2N -C ₆ H ₄ -N=N-C ₆ H ₄ -CHC(CN) ₂	1360	526
6	 NPh_2N -C ₆ H ₄ -N=N-C ₆ H ₄ -C ₂ (CN) ₃	2776	602
7	 Et_2N -C ₆ H ₄ -N=N-C ₆ H ₄ -N=N-C ₆ H ₄ -NO ₂	19000	504
8	 Et_2N -C ₆ H ₄ -N=N-C ₆ H ₄ -N=N-C ₆ H ₄ -C ₂ (CN) ₃	24000	—
9	 MeO -C ₆ H ₄ -C \equiv C-C ₄ H ₃ (NO ₂)S	276	362
10	 NPh_2 -C ₆ H ₄ -CH=CH-C ₄ H ₃ (NO ₂)S	756	458
11	 NPh_2 -C ₆ H ₄ -N=N-C ₄ H ₃ (NO ₂)S	1390	550
12	 CH_3 -C ₆ H ₄ -N=N-C ₆ H ₂ (CH ₃) ₂ -N=N-C ₁₀ H ₆ (OH)	—	518

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Desirably the chromophore employed in the invention has an absorption wavelength from between about 200 nm and about 800 nm, preferably from between about 300 nm and about 600 nm. The preferred chromophores according to the invention also desirably have an effective cis-
5 trans isomerization process when excited at their absorption wavelengths. Also, desirably the chromophores are such that polarization alone can be used to induce alignment in the chromophores (e.g., as described in Rochon et al., "Optically Induced and Erased Birefringence and Dichroism in Azoaromatic Polymers", *Appl. Phys. Lett.* 60, pages 4-5 (1992); Kim et al., "Laser Induced
10 Holographic Surface Relief gratings on Nonlinear Optical Polymer Films", *Appl. Phys. Lett.* 66, pages 1166-1168, (1995)). Optimally this induced alignment will be in the direction to reduce interaction with the incident polarized light.

According to the invention, and, as further described below, a
15 waveguide that exhibits 2°-NLO properties can be obtained not only by chemical conjugation of a 2°-NLO chromophore into a polymer backbone, but also desirably can be obtained by merely mixing a 2°-NLO chromophore with a polymer backbone in a process commonly known as "doping". For "doping" it is preferable that the concentration of the chromophore be between about 3%
20 and about 10% of the total polymer mixture. Other variations such as would be obvious to one skilled in the art are contemplated by the invention.

The chemical structures of certain of the preferred polyimides to be used for the proposed device according to the invention are shown in **Figures 1-3**, with the corresponding absorption spectra of the corresponding polymers
25 being shown in **Figure 4**. These materials provide great flexibility in terms of chemical modification, such modification which may be desirable in optimizing the properties of the polymer for use in optical applications. For instance, in dialkyl amino nitro diazo it is possible to change the electron donor in the chromophore from nitrogen to oxygen and the electron acceptor
30 from nitro to sulfone to get the alkoxy sulfone diazo (Mordant Orange 10). This will shift the absorption of the material from 532 nm to 386 nm as shown in **Figure 4**.

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Therefore, by changing the pendant chromophore in the polyimide employed in the different layers of the device according to the invention, the absorption peaks for each layer can be completely separated, or single layer devices having different optical properties can be obtained. Hence, *inter alia*, the invention renders it possible to manipulate each layer of the polymer films by using the appropriate wavelength to induce refractive index changes. The concentration of chromophores can be carefully adjusted by copolymerization to control the refractive index at the expense of the nonlinearity (e.g., as described in Girton et al., *supra*, and Keil, *supra*).

Furthermore, with active devices, transparent electrodes can be incorporated in the form of transparent layers of Indium-Tin-Oxide ITO. Under proper conditions it can form a thin film on a glass or polymer substrate which is electrically conductive and optically transparent in the ultraviolet to infrared region of the electromagnetic spectrum. It can be deposited as a thin film layer (typically 100 nanometer thickness) using an alloy of Indium and Tin and Oxygen atmosphere by reactive sputtering techniques. Reactive sputtering techniques include DC, RF, and Magnetron sputtering, and are known to those working in the field.

Taking advantage of highly efficient 2°-NLO polymers that have large electro-optic coefficients (e.g., the preferred polyimides depicted in **Figures 1-3**, or other polyimides), the driving voltage for the operation of an active device according to the invention which incorporates such a 2°-NLO should also be low. The novel fabrication processes according to the invention allow the construction of multiple levels or multiple layers on the same board. According to the invention a "board" can be a simple glass substrate or a silicon chip with electronic circuits or any sort of support platform for the polymer films. The multiple levels or layers on the board are individually processed and interconnected to other layers by various means (e.g., directional and grating couplers, and/or inter-connects). By constructing such multi-layered systems, it is possible to fabricate very dense optical integrated circuits (e.g., having more than one function, such as a combination of interconnected circuit elements inseparably associated on or within a continuous substrate), if so desired. A sample board according to the invention is depicted in **Figure 17**.

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The methods of fabricating the novel devices of the invention desirably employ a number of novel photo-processes such as photo-induced (Rochon et al., "Optically Induced Surface Gratings on Azoaromatic Polymer Films", *Appl. Phys. Lett.*, 66, pages 136-138, (1995)), or photo-induced electric-field-assisted (Hill et al., "Reversible Optical Storage Utilizing Pulsed, Photoinduced, Electric-field-assisted Reorientation of Azobenzenes", *Appl. Phys. Lett.* 66, pages 2156-2158, (1995)) poling (apparatus shown in Figure 5) and photobleaching techniques (Figure 11) for writing gratings and waveguides (Keil, *supra*). These processes facilitate the fabrication by producing waveguides using lasers at the absorption wavelength of the 2°-NLO chromophores (e.g., typically between from about 300 nm to about 600 nm). The waveguides are unaffected by light with lowest wavelength outside the range of their absorption, such as at communication wavelengths of from about 1.3 to about 1.5 microns. Additionally, these processes reduce the costs dramatically and provide an easy way to fabricate integrated optical circuits.

With use of the preferred laser writing technique, desirably a holographic grating can be assembled with proper pitch to control the amount of out-coupled light with the appropriate fraction. Also, optionally the destruction of the chromophores by a well established photobleaching process (see, e.g., Rikken et al., "Poled polymers for frequency doubling of diode lasers" *Proc. SPIE*, vol 1337, pp 35 (1990)) using a photo-masking technique that causes a reduction of the chromophores in the material, can be employed to produce efficient waveguides in a preferred process according to the invention.

Gratings on waveguides for light coupling (including the Bragg-Grating discussed previously) have been studied for a number of years (Tamir, ed., "Topics in Applied Physics: Integrated optics", Springer Verlag, Vol. 7, page 92, (1979)), and coupling efficiencies of 80% or more have been achieved for passive couplers by the proper adjustment of waveguide layers and refractive index, n , and groove spacing of the grating, Λ . Making use of the second-order nonlinearity of the waveguides, the refractive index, n , across the grating can be changed by applying a field across the waveguide. This allows the coupling efficiency of the grating to be changed or adjusted. Such a device according to the invention provides an active grating-coupler that also can be employed as a light modulator, a light filter, or even a light valve.

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In particular, the present invention desirably provides a methodology to fabricate "stacked" integrated optical circuits (i.e., circuits that are layered one on top of another instead of side-by-side, or in the same plane). Preferably such circuits are constructed using a unique laser-writing waveguide fabrication technique in accordance with the invention. A stacked device having two or more layers (especially having three layers) and which has independent waveguides and gratings in each layer is particularly preferred according to the invention. A variety of fabrication techniques can be employed to carry out construction of this device, e.g.,: (a) preferably utilizing index anisotropy caused by photo-induced chromophore orientations in 2°-NLO polymers (laser-writing) to fabricate the waveguide and the grating; (b) optionally utilizing the photobleaching process to fabricate the waveguide and the grating; and (c) optimally using a combination of these two techniques. The term "anisotropic" refers to a material whose electrical or optical properties are different for different directions of propagation or different polarizations of a traveling wave.

A device according to the invention can comprise one or more polymer layers as depicted in **Figure 6**. **Figure 6** diagrams a waveguide where the refractive indices n_1 , n_2 , and n_3 , are all different. The layers having these respective indices can comprise either air, buffer, and/or 2°-NLO. A "buffer" can be another polymer or any other material which: (1) has a lower refractive index than the guiding layer and light of the relevant range (i.e., range of chromophore excitation of chromophore employed in the device) passes through unaffected, (2) is employed to separate one layer from another layer or material (e.g., electrode), and (3) is noninterfering with the optical properties of layers above and/or below the buffer layer. Thus, a buffer layer can act merely as a separator and can be, for instance, a polymer such as polyimide, where the polymer (polyimide) does not contain any chromophore. In particular, preferably the buffer is polyimide, PMMA, or polystyrene that does not contain a chromophore.

An especially preferred embodiment according to the invention is the active WDM device having the arrangement shown in **Figure 14**. Thus, among other things, the present invention provides for an "active" Bragg-Grating WDM. Using the polymer with a sulfone diazo chromophore (**Figure 3**), in a first method, the well established photobleaching method desirably can be used to write both the waveguide and the grating (**Figure 11**). In a second method, preferably using the direct laser-

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writing technique, waveguides and gratings in a single-layer polymer can be constructed. Following construction of the single-layer systems, one or more additional polymer layers optionally can be added, and a device or system having two or more stacked polymer layers optionally can be constructed. To construct a second layer, or another layer (i.e., a third, fourth, fifth or other polymer layer), the underlying layer or layers (e.g., the first or other layer(s) constructed prior to the present layer being applied can be protected by a UV absorbing buffer layer such as polymethyl methacrylate (PMMA) or, with use of laser-writing techniques, e.g., employing a polymer which incorporates a different chromophore causing absorption at a different wavelength.

Following construction of a single layer device according to the invention, parameters such as stability, grating-index modulation depth, surface relief index modulation depth, and the effect of each parameter on the resonance condition for in and out-coupling efficiency of the guided wave are evaluated. These parameters confirm the optimal approach for fabrication of a multi-layer optical integrated circuit device capable of performing Wavelength Division Multiplexing (WDM), Add/Drop Multiplexing (OADM) and/or Cross-Connect (OXC) operations. The following accordingly is an outline of some of the physical and theoretical issues that are addressed in practicing and optimizing the invention (although each of the (7) steps below is not strictly necessary, just merely exemplary).

(1) Determination of materials for and synthesis of the suitable material for the waveguide. In particular, use of 2°-NLO polymers, particularly 2°-NLO polyimides (especially polyimide-dialkyl amino nitro azo, polyimide containing sulfone diazo, and polyimide-dialkyl amino nitro diazo) is preferred according to the invention, although other polymer chromophors also can be employed, e.g., as described herein. The proper solvents and concentrations for each material for spin-coating uniform, thin, films on glass substrates needs to be addressed. Generally, however, appropriate coating can be obtained with use of a polymer having a concentration of at least about 300 g/l of N-methyl pyrrole (NMP) or dimethylformamide (DMF). In general, for thick, uniform films, a high boiling point solvent is desirable. Typically according to the invention, the polymer is prepared e.g., in powder form. Subsequently the polymer is dissolved in a suitable solvent (e.g., NMP) and spin-coated on a surface, or adhered to the surface by any appropriate means known in the art. Procedures for

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precipitating the polymer as a powder, washing and drying the polymer, making a high concentration solution (e.g., in 1 to 2 ml of solvent) and spin coating (e.g., onto about a 1.5 x 1 inch surface, such as glass microscope slide) are known in the art (see, e.g., Saadeh et al., *supra*).

5 (2) Guided-wave structure design. A mathematical simulation of the guided wave conditions of different wave guide structures applied to 2°-NLO polymers desirably can be performed. Such simulation optionally takes into account the geometry and material properties such as the difference in the refractive indexes between poled and unpoled polymer films using the different poling methods (laser
10 and corona). For fabrication of complicated circuits, this step may be required. Any appropriate simulation program known and available in the art can be employed (e.g., the product BPM_CAD, Optiwave Corp., ON, Canada; the product Beam Prop, R Soft, Inc., NY, NY; and the product Thor/Prometheus, BBV Software BV, The Netherlands)

15 (3) Construction of specialized apparatus (or modification of an existing apparatus) for waveguide fabrication and testing. As depicted in **Figure 7**, a computer controlled precision X-Y stage apparatus is preferred for laser writing of waveguides, and subsequent testing of waveguides, although other means can be employed. The apparatus desirably can be constructed using commercially available, programmable,
20 high-precision X-Y translation tables. Other components of the apparatus also are commercially available.

 (4) Fabrication of waveguides using, for instance, laser-induced chromophore alignment and photobleaching technique. Also, the same techniques desirably can be employed to write surface-relief gratings in the highly nonlinear polymers with
25 sulfone and diazo chromophores, and to measure the nonlinearity of the waveguide and diffraction efficiency of the fabricated gratings from outside and through the waveguide.

 (5) Analysis of the waveguides (e.g., to determine the effectiveness of the laser-writing technique which induces chromophore alignment to produce index
30 anisotropy) and examination of the gratings, desirably by Atomic Force Microscopy (AFM), or other appropriate means. Also, a determination can be made of the performance of the components fabricated with different methods such as

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photobleaching as compared with photo-induced poling, to determine the optimal means for fabrication of the components for a particular application.

(6) Fabrication of stacked waveguides using the same techniques as in (4) above.

5 (7) Determining the multiplexing and coupling efficiency of the active devices according to the invention as compared to passive devices known in the art (as well as prepared according to the invention). Similarly, an assessment can be made of waveguide loss in the waveguide and through the grating of the novel devices according to the invention. This can be done, for instance, using prism-coupling,
10 along with a near-field fiber-probe technique (which is well-known in the art). The measurements can be repeated for each layer present in a device according to the invention. This determination, of course, is done merely to optimize components for a particular application.

Thus, the present invention optimally provides for construction of a family of
15 components and devices, based on the uniquely designed polymer waveguides according to the invention, which optionally combine the passive WDM of the Bragg-Grating with the nonlinearity of 2°-NLO polymers. In a preferred embodiment, an optical add-drop multiplexer is constructed which also has optical cross-connect properties.

20 The following Examples are by means of illustration, not limitation. Of course, variation of these Examples in the spirit and scope of the invention are contemplated herein.

Example 1: Polymer Synthesis and Preparation of Waveguide and Cladding

25 This Example describes polymer synthesis and preparation of exemplary waveguide and cladding layers.

This Example describes the preparation of two stable cis-trans-active 2°-NLO polymers which have separate and preferably far apart absorption peaks. The absorption spectra of the chromophores used (i.e., sulfone diazo (Mordant Orange 10)
30 chromophore present in a polyimide or poly(methyl methacrylate) host matrix ("A" peak), and dialkyl amino nitro diazo present in polyimide-dialkyl amino nitro diazo ("C" peak)) are shown in **Figure 4**. The materials shown in the **Figure 4** are not the only azo dyes with appropriate properties for use in the invention. Other well-known

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azo dyes such as Disperse-Red exhibit similar properties (Sekkat et al., "Room-Temperature Photoinduced Poling and Thermal Poling of a Rigid Main-Chain Polymer with Polar Azo Dyes in the Side Chain". *Chem. Mater.*, 7, 142-147 (1995)). However, the absorption peak of Disperse-Red is at 480 nm, making it unsuitable to use in conjunction with the material shown in **Figure 4**.

The chromophores are preferably chemically attached to the polymer backbone (e.g., soluble polyimides) for better thermal stability. The nitro-diazo chromophore was chemically attached to the polyimide backbone to produce the polyimide-dialkyl amino nitro diazo polymer shown in **Figure 3**. Synthesis was carried out as described in Saadeh et al., "Polyimides with a Diazo Chromophore Exhibiting High Thermal Stability and Large Electrooptic Coefficients", *Macromolecules*, 30, 5403-5407 (1997).

Chromophores alternately can be physically associated with, but not chemically attached to the polymer backbone, e.g., as wherein the polymer is "doped" with the chromophore of interest. Such a material, polyamic acid doped with sulfone-diazo chromophore is depicted in **Figure 5**. This material was made by mixing sulfone-diazo chromophore with polyamic acid (purchased and used as received from Aldrich Chemicals) and heat-cured at about 200 °C. Sulfone-diazo chromophore was prepared by dissolving Mordant Orange 10 (purchased from Aldrich Chemicals), which is a sodium salt, in water and adding excess amount of HCl to precipitate the sulfone-diazo chromophore.

For making films using polyimide-dialkyl amino nitro diazo, 300 mg of polymer was dissolved in 6 ml of tetrachloroethane. The solution was then filtered with a 0.2 micron filter and the total volume was reduced to 1.7 ml. The solution was then spin-coated on indium-tin-oxide (ITO) substrates. Depending on the spinning speeds, the film thickness ranged between 2 to 5 micron.

For making films using polyamic acid doped with sulfone-diazo chromophore, 36 mg of sulfone-diazo was dissolved separately in 1 ml of N-methyl pyrrole (NMP). This solution was added to 0.5 gram of polyamic acid solution which has 20% polymer content. To this mixture 3.5 ml of NMP was added, the solution was filtered, and the total volume was reduced to 1 ml. Spin-coating at 5000 rpm produced films about 2 to 3 micron thick. These films may then be imidized at 200 °C to form a hard and insoluble film. The insolubility is necessary for multi-layer films.

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Cladding also can be fabricated for the waveguides and optical switches of the invention, e.g., to separate the waveguide from the solid support, or two separate independent waveguides. For fabrication of cladding, the refractive index of a light-guiding layer (i.e., a waveguide) must be higher than the layers above and below it.

- 5 In particular, to fabricate a multilayer optic switch comprised of separate waveguides made of either polyimide-dialkyl amino nitro diazo or polyamic acid doped with sulfone-diazo chromophore, these two guiding layers must be separated by a cladding layer. By imidizing pure polyamic acid, an insoluble layer with lower refractive index than either polyimide-dialkyl amino nitro diazo or polyamic acid doped with sulfone-
- 10 diazo chromophore is formed. The structure is represented in **Figure 6**, wherein in this case, n_1 and n_3 are waveguides, and n_2 is cladding. Optimally, but not depicted in **Figure 6**, the waveguide layer n_3 would be formed on top of another cladding layer, which itself would be supported by the solid support. Still further waveguides (each separated from other waveguides by a cladding layer) could be formed on top of n_1 .
- 15 However, for the waveguiding condition to be satisfied by the multilayer device depicted in **Figure 6**, $n_1 > n_3$ and $n_3 > n_2$.

Some physical measurements of the films produced that are capable of functioning as either waveguide or cladding are shown in **Table 2**.

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Table 2. Physical properties of films produced.

	chromophore %weight	Refractive Index n_{TE} ^a		r_{33} ^d (@1.3 μ m)	Thermal stability	Absorption peak (nm)
		Imidized ^b	not-imidized			
Polyimide- dialkyl amino nitro diazo	39	1.657	N/A	35	180 °C	520
Polyamic acid doped with sulfone- diazo chromophore	37	1.624	1.603	≈ 10 ^c	≈ 180 °C	380
Polyimide (cladding)	N/A	1.588	^c	N/A	N/A	≈ 280 ^f

^a Measured at 632.8 nm wavelength.

5 ^b When imidized, the film thickness is reduced by 25%.

^c Value not measured. The cladding layer is formed by imidizing the poly-amic acid.

^d Optical nonlinearity and thermal stability measured by P.I. at University of Chicago (see Saadah et al).

10 ^e Conservatively estimated value based on the similar azo polymer (Yu et al.: "Novel Second-Order Nonlinear Optical Aromatic and Aliphatic Polyimides Exhibiting High Temperature Stability." *Appl. Phys. Lett.*, 60, 1050-1052 (1995)).

^f Conservatively estimated value.

Accordingly, this Example describes exemplary polymer synthesis and
15 preparation of exemplary films capable of functioning as waveguide or cladding layers.

Example 2: Exemplary Photo-Induced Birefringence Laser Writing in Waveguide Fabrication

20

This Example describes the theoretical basis underlying waveguide design according to the invention employing photo-induced birefringence laser writing, and particularly describes the theoretical bases for this use.

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Polymer waveguides have been fabricated in a number of ways including by photolithography, and photo-crosslinking, among others. Photolithography is probably the most widely used because of the established techniques in the semiconductor industry. In the context of the present invention, photo-induced
 5 birefringence is employed to fabricate waveguides, optimally having the arrangement depicted in **Figure 6**.

For the case in **Figure 6** where n_1 is very much less than n_3 , e.g., n_1 is 1, and n_3 is 1.5 or greater (i.e., an asymmetric waveguide), the required refractive indices have the relationship in refractive index difference (Δn):

$$10 \quad \Delta n = n_2 - n_3 \geq (2m_s + 1)^2 \lambda_0^2 / (32n_2 t^2)$$

where t is the thickness of the waveguide, λ_0 is the vacuum wavelength and m_s is the propagation mode, or guided wave mode) Hunsperger, "Integrated Optics: Theory and Technology", Third Edition, Springer-Verlag, New York. While $m_s=0$ is preferred
 15 according to the invention (lowest mode), higher modes are possible depending on structure, with $m_s=x$, where x is any whole number from 1 to infinity, and desirably, is any whole number from 1 to 10, especially from 1 to 4. Therefore for an asymmetric 3 μm thick sample at 1.3 μm wavelength, $\Delta n=0.003$ will suffice for single mode ($m_s=0$) confinement. This condition can be satisfied by photo-induced birefringence
 20 laser writing (e.g., Rochon et al. (1992), *supra*; Kim et al., *supra*). Increasing the waveguide thickness requires an even smaller Δn to satisfy the beam confinement condition.

Thus, for an asymmetric waveguide as depicted in **Figure 6**, desirably $n_1 < n_2$ and n_3 is $< n_2$. In **Figure 6**, light is carried in the n_2 layer (i.e., the n_2 layer functions as
 25 the waveguide), for this to happen, the index of refraction n_3 and n_1 must be less than the index of refraction n_2 .

For the case where $n_3 = n_1$ (i.e., a symmetric waveguide), for waveguiding of a given mode to occur, the following index condition must be satisfied:

$$30 \quad \Delta n = (n_2 - n_1) \geq \frac{m_s^2 \lambda_0^2}{4t^2 (n_2 + n_1)}$$

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where t , λ_{on} , and m_s are as previously described. This condition for Δn in the case of a symmetric waveguide is easily satisfied by the smallest difference between n_1 and n_2 , a difference which clearly lies within the laser-induced birefringence limits (Yu et al., "Highly Stable Copolyimides for Second Order Nonlinear Optics; *Macromolecules*: 29, pages 6139-6142 (1996); Gharavi et al., "Fine-Tuning Optical Nonlinearity and Thermal Stability in Functionalized Co-polyimides", (presentation), *American Physical Society Meeting*, March 18-22 (1996)).

Accordingly, this Example provides the theoretical basis for use of photo-induced birefringence laser writing in construction of either an asymmetric or a symmetric waveguide according to the invention.

Example 3: Exemplary Direct Laser Writing in Waveguide Fabrication

This Example describes the use of direct laser writing in waveguide design according to the invention.

Certain azo dyes (chromophores) undergo cis-trans isomerization when excited by light within their absorption bands. This cis-trans isomerization continues until the chromophore aligns itself in such a way that the optical absorption is minimized in the chromophore. If the excitation light is polarized the chromophore alignment is in the same direction of the polarization of the light. This condition is referred to as photo-induced birefringence (Rochon et al., "Optically Induced and Erased Birefringence and Dichroism in Azoaromatic Polymers", *Appl. Phys. Lett.* 60, 4-5 (1992); Kim et al., "Laser Induced Holographic Surface Relief gratings on Nonlinear Optical Polymer Films", *Appl. Phys. Lett.* 66, 1166-1168, (1995)), and can be employed according to the invention to write waveguides by purely optical means (i.e., laser-writing).

In particular, the direct writing can be carried out using the cis-trans isomerization property of the property of the azo (e.g., polyimide depicted in Figure 2) and diazo (e.g., polyimides depicted in Figure 1 and 3) chromophores excited at their peak absorption wavelengths, and may be assisted by a corona field. The absorption spectra of the chromophores sulfone diazo (present in polyimide containing sulfone diazo), dialkyl amino nitro azo (present in polyimide-dialkyl amino nitro azo), and dialkyl amino nitro diazo (present in polyimide-dialkyl amino nitro diazo) are depicted in Figure 4, and are, respectively, from about 300 to 450 nm, from

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about 400 to about 500 nm, and from about 425 to about 600 nm. The differences in the absorption peaks apparently are due to the differing conjugation lengths and donor-acceptor groups at each end of the chromophores.

A direct laser writing of waveguides can be performed, for instance, using the apparatus depicted in **Figure 7** to achieve excitation of the different chromophores at their absorption maxima. As shown in **Figure 7**, the sample (10) comprising the particular polyimide(s) layered on a solid surface such as silica or glass is mounted on an X-Y stage (20) present on an optical table (30). The X-Y stage is employed to follow the path of the waveguide. The entire structure of the X-Y stage and sample are placed in a nitrogen hood (40) to allow the onset of corona discharge (50) with use of the high voltage supply (60). The nitrogen hood is merely a transparent enclosure for confining the gas used for corona discharge (e.g, nitrogen, argon, helium, etc.), and further contains a port for entry of the laser beam to excite the chromophores. As depicted in **Figure 7**, a laser (70) is employed to create the beam (80), which is then focused on the sample with use of one or more lenses (90) and mirrors (100), and is monitored by way of a beam monitor (110). The X-Y stage is controlled with use of computer (120), as depicted in **Figure 7**.

Using the apparatus depicted in **Figure 7**, the surface of the polymer will be charged at room temperature using a corona discharge under nitrogen atmosphere. Under the force of the external field of the charged surface, the chromophores will align along the field direction perpendicular to the plane of the film. At room temperature, however, this alignment will simply disappear due to the elasticity of the polymer matrix. This phenomenon is shown in **Figure 8**, which depicts chromophore alignment of polyimide-dialkyl amino nitro diazo, as measured by in situ second harmonic generation (SHG; arbitrary units) at room temperature over the course of 2000 seconds (demonstrated at the University of Chicago, Doctors Alireza Gharavi and Luping Yu). As can be seen in **Figure 8**, the intensity of the second harmonic light generation increases with the onset of corona discharge ("Corona ON") and falls off with the termination of corona discharge ("Corona OFF").

Multiple cis-trans isomerization accompanying excitation of the chromophores at their absorption maxima will overcome this elasticity, and will essentially "fix" the chromophore alignment in place. Thus, after tracing the waveguide pattern by the

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writing laser upon removal of the corona discharge field, the chromophores will remain aligned only in the laser-written pattern, and the waveguide will be formed.

Accordingly, this Example provides the use of direct laser writing in waveguide design according to the invention. Of course, given that polymers
 5 incorporating chromophores having different absorption maxima can be employed according to the invention, this method can be employed for the direct laser writing of stacked waveguides comprising more than one polymer layers.

Example 4: Exemplary Direct Laser Writing Not Involving Corona Discharge

10 This Example describes another illustration of the use of direct laser writing in waveguide design according to the invention.

Instead of the apparatus employed in the prior Example, the apparatus **Figure 9** can be employed to write waveguides using the laser-writing technique. The X-Y stage has a resolution of 0.1 μm . Several computer programs in Basic programming
 15 language were written to control the stage for writing waveguides and gratings.

The exemplary waveguide written is the symmetric waveguide where top and bottom cladding layers and either side of the waveguide have the same refractive index. In this case, for waveguiding of a given mode to occur, the following index condition must be satisfied (Hunsperger, Robert G., *Integrated Optics: Theory and*
 20 *Technology*, Third Edition, page 101, Springer-Verlag (1991)):

$$\Delta n = (n_2 - n_c) \geq \frac{m_s^2 \lambda_o^2}{16t^2(n_2 + n_c)}$$

25 where n_2 and n_c are the refractive indices of the guide and cladding, t is the thickness of the guiding layer, λ is the wavelength of the guided light, and m_s is any odd whole number from 1 to infinity. For a 4 μm film of approximately 1.6 refractive index at 1.3 μm , the minimum change in the refractive index is about $\Delta n=0.002$. This condition is
 30 easily satisfied by the smallest difference between n_2 and n_c , most certainly lying within the laser-induced birefringence limits (Yu, D., Gharavi, A., and Yu, L., "Highly Stable Copolyimides for Second Order Nonlinear Optics; *Macromolecules*; 29, pages 6139-6142 (1996); Gharavi, A., Yu, D. and Yu, L., "Fine-Tuning Optical Nonlinearity

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and Thermal Stability in Functionalized Co-polyimides", (presentation). *American Physical Society meeting*, March 18-22 (1996)).

In an exemplary experiment according to the invention, a photo-induced birefringent waveguide in a sulfone-diazo polymer was written. To maximize Δn between the core and the cladding, first a 100 μm track was combed with TE (Transverse Electric vector) polarization parallel to the plane of the polymer film using a helium-cadmium (HeCd) laser at 442 nm, to align the chromophores in the plane of the film. The width of this track determined by the beam spot at the sample was about 300 μm . By focusing the laser beam at the middle of the combed track and reducing the intensity of the beam to avoid burning the sample, the chromophores were aligned perpendicular to the plane of the film. This produces the maximum Δn due to the alignment of the chromophore in different directions. The effect is clearly visible using a polarizing microscope. It can be confirmed using crossed polarizers that the chromophores in the combed track are aligned in the plane of the film while the chromophores in the waveguide are perpendicular to the plane of the film (data not shown).

The combed track was written with 51 mw HeCd laser at 442 nm with a stage speed of 5 $\mu\text{m/s}$. The waveguide was written with a speed of 500 $\mu\text{m/s}$ and laser power of 35 mw. The 442 nm wavelength lies to the right of the absorption peak of the polyamic acid doped with sulfone-diazo chromophore, as described in Example 1.

The effects of tuning the writing beam to the absorption maximum are not evident. On one hand, due to higher absorption, the alignment may proceed faster. On the other hand, due to higher absorption, the beam may not penetrate the depth of the film. At the same time, the other wavelength available at 632.8 nm, of a Helium-Neon laser has no effect on the sulfone-diazo material but lies at the edge of the absorption band of the polyimide-dialkyl amino nitro diazo polymer. In both cases the effect of wavelength and power on chromophore alignment can be further characterized.

Similarly, laser-written waveguides may be written in polyimide-dialkyl amino nitro diazo polymer using a 632.8 nm laser beam. In this case a HeNe laser with 6 mw of output power was used. The combed track was written with TE polarization parallel to the plane of the film at a stage speed of 12 $\mu\text{m/s}$. The waveguide was

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written setting the TE polarization perpendicular to the plane of the film and a stage speed of 500 $\mu\text{m/s}$. This will give the chromophore-alignment arrangement wherein the chromophores in the combed track are aligned in the plane of the film while the chromophores in the waveguide are perpendicular to the plane of the film (data not shown).

Accordingly, this Example provides another illustration of the use of direct laser writing in waveguide design according to the invention. This method can be employed for the direct laser writing of stacked waveguides comprising more than one polymer layers.

10

Example 5: Holographic Grating Formation

This Example describes the formation of gratings in the polymer-based waveguides according to the invention by holographic means.

Gratings are formed by holographic means with use of two laser beams interfering at the 2°-NLO polymer. The period of the grating, Λ , is given by the following formula:

$$\Lambda = \frac{\lambda/n}{2 \sin \alpha}$$

where α (depicted in Figure 10) is the angle between the two intersecting beams, and n is the index of refraction of the material at the wavelength, λ (Yariv, *Optical Electronics*, Forth Edition, Saunders College Publishing, page 548, (1991)).

Therefore, with the proper choice of λ and α , a grating can be written in the polymer material.

If λ is in the UV range, such as the UV line of the HeCd laser at 325 nm, the grating produced will be periodically bleached. If λ is in the absorption range of the chromophore, surface relief gratings are produced. The passive Distributed Bragg Reflector (DBR) will consist of a bleached grating formed using two overlapping beams. The grating period, Λ , is adjusted so that the incident beam is reflected by the periodic perturbation of the grating. Gratings with periods of about 0.4 micron have been fabricated using the above technique in NLO polymer films. The performance of one such grating where the period was measured by moving the grating formed against the interference pattern and measuring the intensity modulation of the

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diffracted light. The average period of the grating (Λ) is measured from a graph of this information to be 0.55 micron.

The distance of arm "b" is adjusted to make a grating with a different period:

$$\alpha = \tan^{-1} \left(\frac{b \sin \beta}{h - b \cos \beta} \right)$$

5

Symbols are defined in **Figure 10** where h and β are constants. The experimental and calculated results are tabulated in **Table 3**. As it can be seen in **Table 3** the calculated and experimental results are in close agreement. Therefore to obtain a grating with a certain period the arm "b" needs to be set to corresponding value. For example, to

10 obtain the grating of **Figure 15**, the arm "b" was set to 130 mm.

Table 3. The variation of the grating period

b (mm)	Λ (calculated) μm	Λ (experimental) μm
23	3.85	3.69
25	3.52	3.72
50	1.77	1.67
80	0.97	0.96
110	0.67	0.67
116	0.62	-- ^a
130	0.55	0.55
150	0.46	-- ^a
170	0.40	-- ^a
190	0.35	-- ^a

15 ^a value not measured

Thus, this Example describes the manner by which gratings can be formed in the polymer-based waveguides of the invention.

20

Example 6: Exemplary Photobleaching in Waveguide

Fabrication and Grating Formation

This Example describes the use of photobleaching in waveguide fabrication according to the invention. Such photobleaching has been successfully implemented

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for other polymer structures (Keil, *supra*; Rikken et al., "Poled Polymers for Frequency Doubling of Diode Lasers", *Proc. SPIE* 1337 (1990) 35).

This process of photobleaching is depicted in **Figure 11**. Typically, a metallic mask (e.g., chromium coated quartz mask, (150)) is made by patterning the shape of the waveguide on a Cr-metal coated thin quartz slide using an etching technique, e.g., photolithography or excimer laser ablation. The mask also can be obtained commercially (Metrigraphics, Division of Dynamics Research Corporation, Wilmington, MA 01887). This mask is then placed on the surface of the polyimide film or other appropriate polymeric material (140), and irradiation (160) is carried out using ultraviolet light from a laser source such as a mercury lamp or a nitrogen or excimer laser. The waveguide is protected from UV radiation by the patterning on the mask, such that the chromophores are preserved in the region of the waveguide alone (170), and are destroyed outside the region of the waveguide (180). This causes a higher refractive index and thickness in the waveguide than in the UV-exposed regions of the polymer film (see, e.g., Ito et al., *supra*, Lindsay et al., *supra*, Edelman et al., *supra*). What results from this process is an unbleached waveguide (170), and bleached polymer (180) in the area surrounding the waveguide. In another step (described in Example 4) or other appropriate means, grating formation can be accomplished by creation of the grating using, for instance, a laser.

For exemplary studies herein, quartz masks were purchased from Photo Sciences Inc. in Torrance, California, with the pattern of the desired waveguides in the form of the fine Cr-metal lines (10 micron wide) drawn on the masks. The mask was then placed on the surface of a spin-coated film, clamped tightly and placed under a UV grid lamp for UV irradiation. The best results were obtained with film thicknesses of 1-2 microns. Thicker films do not bleach properly and thinner films bleached too much. This way a rib waveguide is obtained. The exposed areas shrink in thickness. Since the waveguide itself is protected by the mask, its thickness remains unchanged.

The bleaching times of from about 10 to about 20 hours gave the best results depending on thickness. Longer exposure times dramatically altered the host material, causing rough guide walls. The simplest condition to meet for single mode guiding in a rib waveguide is given by the formula:

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$$\frac{w}{h} \leq 0.3 + \frac{t/h}{\sqrt{1 - (t/h)^2}}$$

5

where "h", "w", and "t" are, respectively, as depicted in Figure 12, the height of the non-bleached portion of the polymer layer, the width of the non-bleached portion of the polymer layer, and the height of the bleached portion of the polymer layer
 10 (Fischbech et al., "Design concept for singlemode polymer waveguides", *Electronic Letters*; 32, 212-213 (1996)).

For ease of handling and light coupling into the waveguide a large cross-section is desirable. Accordingly, lines 10 microns wide were chosen for the masks. Depending on the host material the thickness shrinkage due to UV radiation is about
 15 25%. For example in a UV-treated sample of nitro-azo polyimide, the bleached film of a nitro-azo polyimide shows a 23% reduction in the thickness with a refractive index change of 6% ($\Delta n \sim 0.1$), as determined from the data shown in Table 4.

Table 4

Area	n_{TE}	n_{TM}	Thickness
Unbleached	1.7036	1.6922	2.1 micron
Bleached	1.6031	1.5889	1.6 micron

20

For the above sample, $w=10$, $h=2.1$ and $t=1.6$ micron. These values satisfy the single-mode waveguiding condition of the Equation depicted above.

Accordingly, this Example provides the use of photobleaching in waveguide fabrication according to the invention.

25

Example 7: Exemplary Stacking of Multiple Layers in Waveguide Fabrication

This Example describes waveguide fabrication according to the invention by the stacking of multiple polymer layers.

To stack multiple waveguide layers and gratings, a device must be constructed
 30 one layer at a time. Fabrication needs to be carried out such that the fabrication of the top layer does not interfere with, or deleteriously effect, fabrication of the bottom layer, or other lower layers. Consequently, prior to the present invention, use of the photobleaching technique only could be employed for the bottom layer of

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multilayered devices, or for single layer devices, or for multilayered devices where the layers are employed in a side-by-side (i.e., non-stacked) position. By comparison, the laser writing technique of **Figure 7** as applied in the present invention is completely non-interfering with layers other than the layer being written.

5 For instance, a bottom layer can be constructed with polyimide containing sulfone diazo, which has an absorption maximum at about 386 nm (**Figure 4**). The next layer could comprize either polyimide-dialkyl amino nitro azo or polyimide dialkyl amino nitro diazo, which each have an absorption maximum at a longer wavelength. A third layer, or other layers (if present), could comprise a polymer
10 exhibiting a different absorption maxima than the polymers present in the other layers. Use of the polymers in this fashion has the net result that the fabrication of layers in addition to a first layer will not interfere with, or destroy, the structure of the first (bottom) layer, or other lower layers.

Thus, this Example provides a method of waveguide fabrication by the
15 stacking of multiple polymer layers.

Example 8: Passive and Active Devices

This Example describes the construction of passive and active devices according to the invention.

20 **Figure 13** depicts a passive multiplexer according to the invention which consists of two waveguides (n_1 and n_3) connected by a holographic bleached or "surface relief" grating, and buffer (n_2). The configuration alternately could be either stacked or side-by-side. As set out in **Figure 13**, two wavelengths enter as λ_1 and λ_2 , and encounter a grating which is made to reflect one beam at a specific angle and then
25 let all others pass through, such that n_1 is reflected at a specific angle (θ) onto another waveguide, and passes through unimpeded. In **Figure 13**, λ_1 is reflected at an angle (i.e., the "angle of incident reflection" or "angle of reflection") such that it is accepted by the adjacent waveguide. A grating (as depicted in **Figure 13**) is formed in the n_2 layer; the other possibility is that of a grating formed in the n_1 layer. If light has the
30 appropriate angle it will be guided through the n_3 layer, if not, it will pass through. Therefore for a passive device, the angle of reflection must be precisely controlled by the material (i.e., grating period) and the nature of the material. The angle of reflection depends on the period of the grating and the refractive index of the medium.

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By comparison, for an active device, the angle of incident reflection can be adjusted by applying a voltage. Therefore in a passive device, just the path of light is changed, all other properties remain the same. There may be other side reflections of λ_1 , e.g., at smaller intensities. These can be captured, e.g., in another device such as switch, etc., or can merely be ignored.

The method of the present invention also allows the fabrication of the active devices depicted in **Figures 14 and 15**. When the grating is in cladding (i.e., in buffer), an active device is not obtained, since the grating would not respond to an electric field. When the grating is in n_1 , an active device is produced. This situation is described in **Figure 14**. In this case, control of the angle of reflection is achieved by applying voltage. Voltage changes the refractive index of the 2°-NLO material. Thus, **Figure 14** depicts an active three-layer device where n_1 and n_3 are made of different 2°-NLO polymers (e.g., polyimide-alkoxy sulfone diazo, polyimide-dialkyl amino nitro azo, and/or polyimide-dialkyl amino nitro diazo) and the refractive index can be changed by applying a field across the waveguide. Desirably, with such a two layer device, the layers are made up of 2°-NLO polymers that include the sulfone diazo and nitro-diazo chromophores.

Figure 15 depicts a double grating "resonance matched" multiplexer, where n_1 and n_3 are made of different 2°-NLO polymers (e.g., polyimide-alkoxy sulfone diazo i.e., modified (Mordant Orange 10), polyimide-dialkyl amino nitro azo, and/or polyimide-dialkyl amino nitro diazo).

In **Figure 15**, both n_1 and n_3 are waveguides; both are active and both have gratings. This makes it easier to couple light into the other waveguide since there are two levels at which the angle of the incident reflection can be controlled. In both **Figure 14 and Figure 15**, n_2 is the index of refraction of a buffer layer. Wavelengths λ_1 and λ_2 flow in the first waveguide, n_1 . A small bias across the electrodes (+/-) will induce a refractive index change in the Nonlinear Optical (NLO) grating, filtering one of the channels, and coupling it into the second waveguide, n_3 .

The gratings in the active devices in **Figures 14 and 15** optimally are formed by holographic means. A passive device accordingly can be constructed consisting of a bleached grating formed as described above. The grating period, Λ , can be adjusted so that the angle of incident reflection (or angle of entry into another layer, labeled Φ_m

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in Figure 13) matches the acceptance angle of the n waveguide (i.e., n_2 in Figure 13).

This concept of having a gratings' properties (i.e., ability to reflect light at a particular angle) changed by an electric field is novel. The ability to control this angle provides for "tunability". It also is possible to control the intensity of the light that is switched

5 by the optical switch of the invention.

Accordingly, this Example describes the manner by which passive and active devices can be formed according to the invention.

Example 9: Basic Grating-Coupler Theory in Waveguide Fabrication

10 This Example describes the theoretical basis of grating construction according to the invention.

The energy (e) of a guided wave is scattered by the harmonic perturbation of the waveguide by grating into space harmonic fields that vary according to the formula:

15

$$e^{i(k_x x - \omega t)}$$

where x is the coordinate in the x direction, ω is the optical angular frequency, t is time, and k_v is the planewave propagation factor in the medium. The value k_{xv} is related to the grating period, Λ , according to the formula:

20

$$k_{xv} = \beta_v + i\alpha = \beta_0 + (2v\pi/\Lambda) + i\alpha$$

where α is the waveguide constant, β_v is the propagation factor of coupled light, β_0 is the surface wave propagation factor, and v is either 0 or any positive or negative

25 whole number ranging from 1 to infinity, and desirably, is any whole number ranging from 1 to 0 (Tamir et al., "Analysis and Design of Grating Couplers", *Appl. Phys.* 14, 235-254 (1977)).

The grating-perturbed waveguide-modes have a set of spatial harmonics with z-direction propagation that is given by:

30

$$\beta_v = \beta_0 + \frac{v2\pi}{\Lambda}$$

$$\beta_v = kn_1 \sin \Phi_m$$

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where Φ_m is the angle that corresponds to the specific waveguide modes that propagate from the lower waveguide into the upper waveguide (Robert G. Hunsperger, *Integrated Optics: Theory and Technology*, Third Edition, page 101, Springer-Verlag (1991)), β_0 is the fundamental factor equal to β_v for any particular mode in the waveguide away from the grating, and other variables are as described previously.

Therefore, for the passive multiplexer, the output angle for wavelength λ_i in layer n_1 can be adjusted to the input coupling angle of the waveguide n_3 ; and because only a single beam into the upper layer is desired, $v = -1$ and the governing equations become:

$$kn_1 \sin \Phi_m = \beta_0 - \frac{2\pi}{\Lambda}$$

where all variables are as previously described (Tamir et al.(1977), *supra*).

Based on the foregoing, it is feasible to stack layers of waveguides and gratings as shown in the active devices in Figure 15 (and Figure 14) to obtain wavelength selective coupling from one waveguide to another by the proper adjustment of Λ and the refractive indices.

Furthermore, making use of the Pockels effect, the refractive index of the 2^o-NLO polymers can be changed by an applied external field according to the formula:

$$\Delta n_{TE} = n_{TE}^3 r_{13} E / 2 \quad \text{and} \quad \Delta n_{TM} = n_{TM}^3 r_{33} E / 2$$

where r_{13} is the electrooptic tensor coefficient, E is the applied electric field, n_{TE} is the refractive index of transverse electric wave, Δn_{TE} is the change in medium refractive index of transverse electric wave, n_{TM} is the refractive index of transverse magnetic wave, Δn_{TM} is the change in medium refractive index of transverse magnetic wave, and r_{33} is the electrooptic coefficient with the units of picometer/volt. (Levy et al., "Reflection Method for Electro-optical Coefficient Determination in Stratified Thin film structures", *Mol. Cryst. Liq. Cryst. Sci. Technol.- Sec. B: Nonlinear Optics*, 4, Pages 1-19 (1993); Reinisch et al., "Fast Pockels Light Modulator Using guided wave resonance", *Applied Optics*, 24, 2001 (1985)). The Bragg wavelength is given by

$$\lambda_B = 2\Lambda n \quad \text{and} \quad \Delta \lambda_B = 2\Lambda \Delta n$$

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(assuming grating period, Λ , constant). Therefore as n shifts so does λ_B . Of course the higher the second-order nonlinearity, the larger the shift in λ_B .

If the grating is designed for resonance coupling for the wavelength λ and angle θ , then a small bias across the grating will shift the resonance enough so that the coupling will not occur. If the grating is designed so that the coupling is slightly off resonance, a small bias across the grating will change the index of the 2°-NLO waveguide to "tune in" to the resonance condition for wavelength λ . This configuration, therefore, can act as a multiplexer or, conversely, demultiplexer, as a modulator, a filter, and a reflector. The bandwidth of a given channel in the 1.5 μm optical communication band is typically a fraction of a nanometer. Therefore the active grating will have to be able to tune over the range of a nanometer. Assuming a 2 μm thick film and using polyimide-dialkyl amino nitro diazo with an r_{33} of 35 pm/V and a grating period, Λ , of 0.3 μm and wavelength of 1.5 μm the applied voltage across the film will have to be 38 volts to give a tunability of 1 nm.

This Example accordingly provides the theoretical basis of device construction (particularly grating construction) according to the invention.

Example 10: Exemplary Design Procedures in Waveguide Fabrication

This Example describes design procedures in waveguide fabrication according to the invention.

In view of the principles discussed in the preceding Examples, optimally the waveguide parameters such as desired thickness and width of the waveguide for a particular application are determined, as a first step. For the first layer of the polymeric material (e.g., comprised of sulfone diazo or other appropriate 2°-NLO), a waveguide is constructed on the substrate using the laser writing technique. The success of this step is determined by measuring the optical loss in the waveguide. For this stage, generally a loss of about 5 db/cm or less is tolerable. For a given wavelength and refractive index, the grating pitch are calculated according to the grating theory described in the earlier Examples. Surface-relief gratings can be written by the holographic technique shown in Figures 10 and 11. When at resonance, such gratings will dramatically increase the losses in the waveguide by leakage through the grating. This provides coupling action where one layer loses a

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wavelength as the other gains it. Upon the successful completion of the first layer, a transparent thin layer of conducting material such as indium-tin oxide (ITO) is deposited on the grating before the deposition of the second layer. The ITO layer can function as a transparent electrode.

5 A second layer of the polymeric material with absorption further into the red region of the electromagnetic spectrum is constructed according to **Figures 16A-B**. The layers are engineered such that the light from the first grating exits with proper angle such that it couples into the top waveguide. Biasing the transparent electrode allows fine-tuning of the resonance condition. To increase the efficiency of light
10 coupling between the waveguides, a grating with a pitch calculated from the equations described in the preceding Example is written in the top grating according to the resonance conditions. This resonance condition is determined by the emerging angle of the light from the first grating. This angle can be measured experimentally.

 In the passive/active multiplexer with "resonance matched" double grating
15 configuration, as shown in **Figure 15**, the top (n_3) and the bottom (n_1) each consist of different 2°-NLO polymers. These chromophores have absorption peaks that are far enough apart to only effect one polymer material at a time during laser-writing of waveguides. It is then possible to efficiently write surface-relief gratings independently.

20 This Example accordingly describes design procedures for waveguide fabrication according to the invention.

Example 11: Exemplary Coupling Techniques

 This Example describes coupling techniques according to the invention.

25 Typically, any of three coupling techniques can be employed to couple light into waveguides: (1) Prism coupling; (2) End coupling; and (3) Grating coupling.

 Prism couplers are frequently used for the input or output coupling of signals into the waveguide layers. As an input coupler, efficiencies between 80 to 100% have been achieved using prism couplers. Each coupled mode is launched at a specific
30 incident angle. Therefore, it is possible to launch a specific guided mode in the waveguide with use of a prism coupler. Furthermore, as an output coupler, each guided mode will exit at a specific angle. Prism coupling was found to be the most effective and reproducible method for coupling light into the waveguides. A prism

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coupler can also measure the thin film parameters of the guiding medium. The thickness measurements were initially performed with a commercial prism coupler (Meticon 2020). Waveguiding characterization was not possible with that system, therefore a multi-purpose setup was constructed to make thickness and refractive index measurements along with light-coupling into the film.

The typical coupling efficiency of the prism coupler employed was found to be between 2-4%. The coupling modes spectrum of a pure polyimide film obtained from the prism coupler was obtained (data not shown). The film thickness and refractive indices were calculated using a computer program with the given modes (Ulrich et al., "Measurement of Thin Film Parameters with a Prism Coupler", *Applied Optics*, 12, 2901-2908 (1973)). It also was possible to fit the data obtained from the coupling modes spectrum to the reflection equations of a multi-layer system to obtain the optical parameters of the underlying films or for multiple-layer systems (Yacoubian, A et al., "Enhanced optical modulation using azo-dye polymers", *Applied Optics*, 32, 3073-3080 (1993)).

End coupling also was employed. However, to obtain efficient coupling, extremely smooth and polished ends of the waveguide are required. In this method the laser beam was focused on the polymer film edge and light was coupled into the film.

This Example thus provides an illustration of a variety of coupling methods that can advantageously be employed in the invention.

Example 12: Exemplary Applications and Uses

The products and processes that comprise the invention advantageously can be applied to many uses, more than are recited herein, and such as would be apparent to one skilled in the art. However, the foregoing description and Examples provide the necessary inventive rudiments allowing (with ordinary skill and knowledge in the art) the establishment of the detailed procedures needed to fabricate waveguides and micro-electrooptic components including, but not limited to, customized gratings to perform a specific task. This paves the way for fabrication of optical integrated circuits. The invention allows determination of the composition-process relationship of the polymeric material used to increase fabrication efficiency. This allows development of multiplexers/demultiplexers and other devices.

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The potential use of a compact, inexpensive, active multiplexer/demultiplexer, and other devices as described herein is readily evident. Their use in the private sector will range from communication and information systems, to future optical switching and computing, to display panels.

5 A sample preferred embodiment is set out in **Figure 17**. This is a 4X4 multiplexer/demultiplexer and cross-connect device according to the invention. The device comprises an optical circuit board (210) having one or more than one (e.g., potentially millions) of optical switches, electrical connections (220) for supplying voltage, input optical fibers (230) to the circuit board, and output optical fibers (240)
10 from the circuit board.

All of the references cited herein are hereby incorporated in their entireties by reference.

15 While this invention has been described with an emphasis upon a preferred embodiment, it will be obvious to those of ordinary skill in the art that variations in the preferred composition and method may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit
20 and scope of the invention as defined by the following claims.

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WHAT IS CLAIMED IS:

1. An optical waveguide comprised of the polymer depicted in Figure 1 or Figure 3, or the doped polymer depicted in Figure 5.

5

2. In an optical switch, the improvement comprising the inclusion of a plurality of layers each comprising an optical nonlinear second-order polymer, wherein the optical nonlinear second-order polymer present in each layer differs from that present in any other layer in terms of its absorption maximum.

10

3. The optical switch according to claim 2, wherein said layers are separated from each other by either a grating or a cladding layer.

4. An optical switch comprising:

15

(a) at least two layers that each comprise an optical waveguide made of an optical nonlinear second-order polymer; and

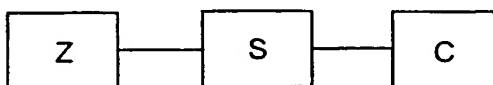
(b) at least one grating,

with the proviso that the optical nonlinear second-order polymer present in each layer differs from that present in any other layer in terms of its absorption maximum.

20

5. The optical switch according to claim 4, wherein said optical nonlinear second-order polymer present in each layer is selected from a polymer that:

(a) has the structure



25 wherein Z is a polymer backbone, S is a spacer attached to Z, and C is an optical nonlinear second-order chromophore attached to S;

(b) is depicted in Figure 1 or Figure 3;

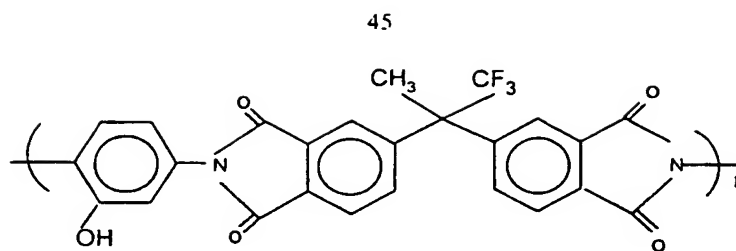
(c) is a polymer doped with a chromophore; and

(d) is depicted in Figure 5.

30

6. The polymer according to claim 5, wherein Z is

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where n ranges from about 20 to about 600.

7. The polymer according to claim 5, wherein Z is selected from the group consisting of Poly(methyl methacrylate), Polystyrene, Poly(p-hydroxystyrene), Polycarbonate, Polyester, Polyurethane, Poly(phenylene vinylene), Polyquinoline, Polyamide, Polyamic Acid, and Polyimide.

8. The polymer according to any of claims 5 to 7, wherein S is a carbon chain comprising from 0 to 30 atoms.

9. The polymer according to any of claims 5 to 8, wherein S is a carbon chain comprising from 2 to 6 atoms.

10. The polymer according to any of claims 5 to 9, wherein C is selected from the group consisting of sulfone diazo, dialkyl amino nitro azo, and dialkyl amino nitro diazo.

11. The polymer according to any of claims 5 to 10, wherein C is any chromophore selected from the group consisting of chromophores present in Table 1.

12. The optical switch according to any of claims 2 to 11, wherein said switch is a device selected from the group consisting of an optical wavelength division multiplexer, an optical wavelength division demultiplexer, an optical add/drop multiplexer, and an optical inter-connect device.

13. The optical switch according to any of claims 2 to 11, wherein said switch has the structure depicted in Figure 13.

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14. The optical switch according to any of claims 2 to 11, wherein said switch has the structure depicted in Figure 14.

15. The optical switch according to any of claims 2 to 11, wherein said switch has the structure depicted in Figure 15.

16. The optical switch according to any of claims 2 to 11, wherein said switch comprises:

- (a) two layers that each comprise an optical waveguide made of an optical nonlinear second-order polymer; and
- (b) one grating.

17. The optical switch according to any of claims 2 to 12 and 15, wherein said switch comprises:

- (a) two layers that each comprise an optical waveguide made of an optical nonlinear second-order polymer; and
- (b) two gratings.

18. The optical switch according to any of claims 2 to 12 and 14 to 17, wherein said switch is active.

19. The optical switch according to any of claims 2 to 13, wherein said switch is passive.

20. The optical switch according to any of claims 2 to 19, wherein said switch further comprises one or more cladding layers.

21. The optical switch according to any of claims 9 to 18, wherein the angle at which said grating transfers optical signals from one waveguide to another can be controlled.

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22. The optical switch according to any of claims 2 to 12 and 15 to 17, wherein the intensity of the optical signal which said grating transfers from one waveguide to another can be controlled.

5 23. The optical switch according to claim 20, wherein said one or more buffer layers comprise at least one grating.

24. The optical switch according to any of claims 2 to 23, wherein said layers are stacked.

10

25. A method of producing an optical switch according to any of claims 2 to 23, wherein said method comprises the use of a fabrication technique selected from the group consisting of laser writing, photobleaching, photo-induced or photo-induced electric field assisted poling, and index anisotropy.

15

26. A method of producing an optical switch according to any of claims 2 to 23, wherein said method comprises the steps of:

(a) obtaining one or more layers of optical nonlinear second-order polymer, wherein each polymer comprises a chromophore that differs from chromophores in other layers in terms of its absorption maximum;

20

(b) subjecting said one or more layers to a beam of irradiation wherein chromophores present in the path of said beam are irradiated, and chromophores not having absorption at the wavelength of the beam are not, said irradiation producing alignment of said chromophores and thereby inducing a change in the refractive index of said one or more layers; and

25

(c) maintaining said one or more layers under conditions such that the irradiated chromophores remain aligned and the chromophores that were not irradiated do not align such that said waveguide is obtained.

30 27. The method of claim 26, further comprising treating said one or more layers with corona discharge to assist with said alignment.

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28. A method of transmitting an optical signal, said method comprising switching said signal from one waveguide to another by virtue of changing the refractive index of a grating through which said signal is transmitted by application of an electric field.

5

29. A method of transmitting an optical signal, said method comprising use of an optical waveguide according to claim 1.

30. A method of transmitting an optical signal, said method comprising use
10 of an optical switch according to any of claims 2 to 24.

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2/11

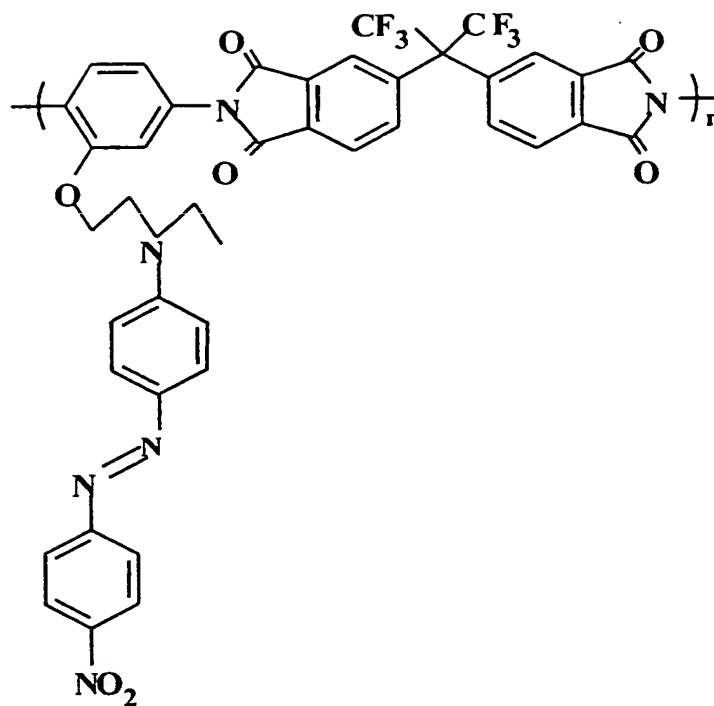


FIGURE 2

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4/11

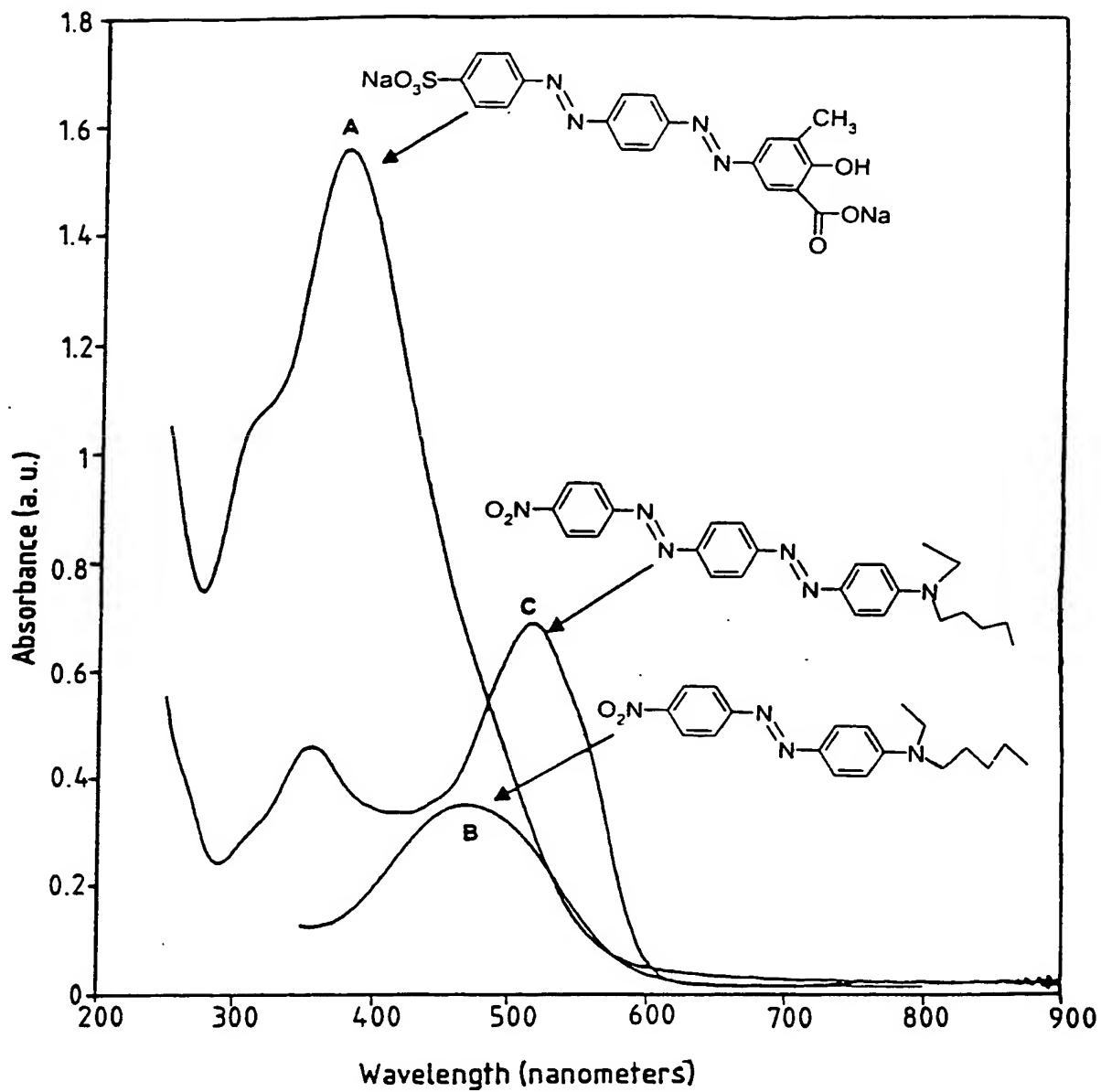


FIGURE 4

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6/11

	n_1
	n_2
	n_3

FIGURE 6

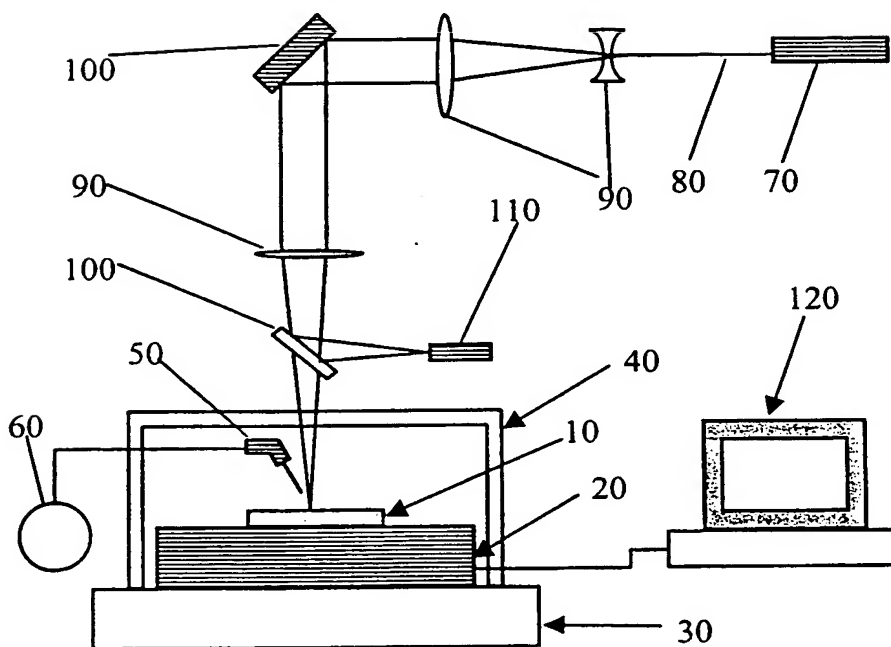


FIGURE 7

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8/11

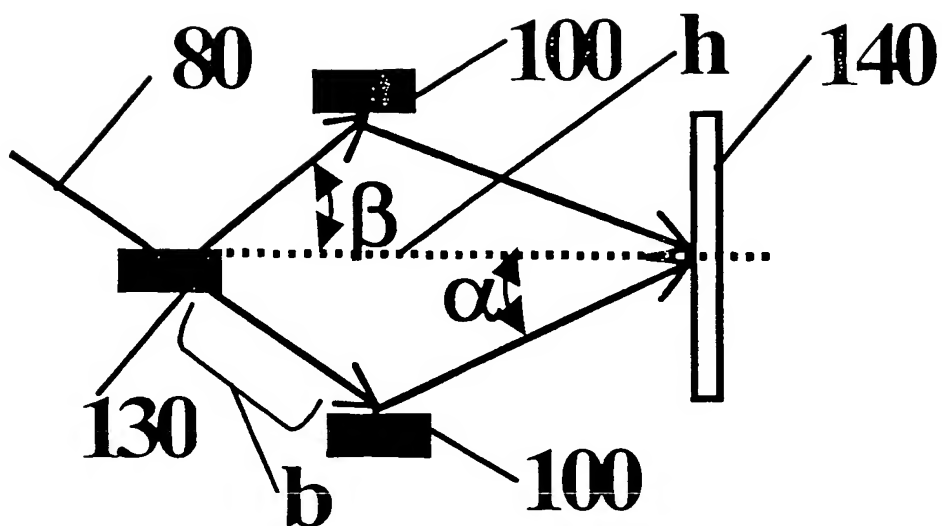


FIGURE 10

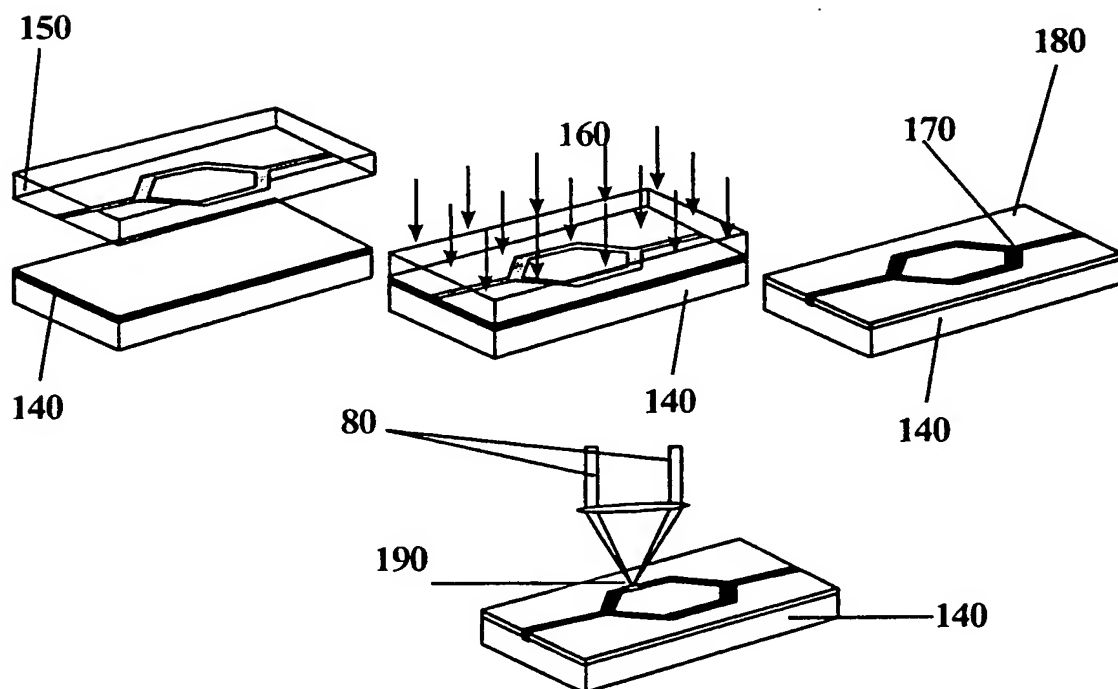


FIGURE 11

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10/11

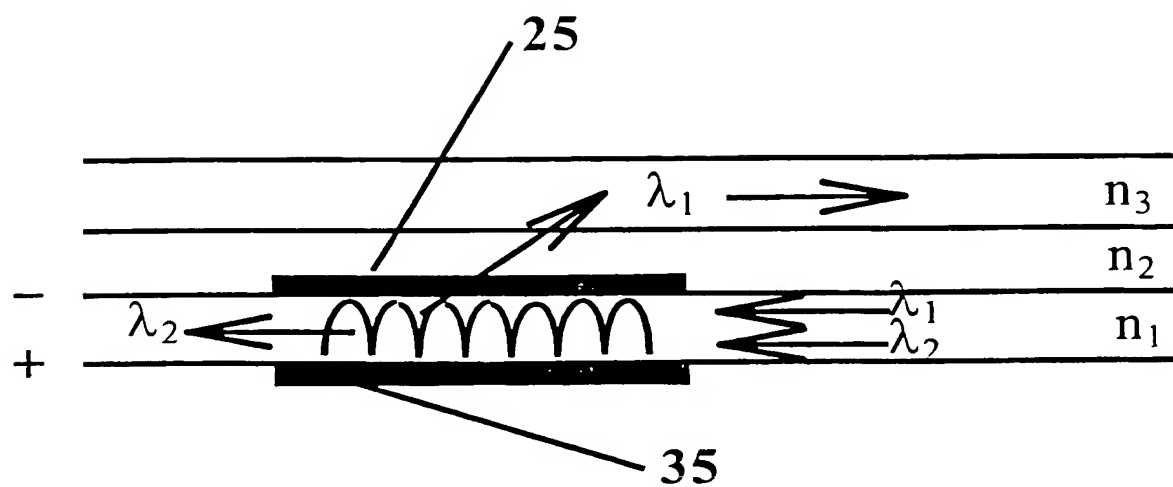


FIGURE 14

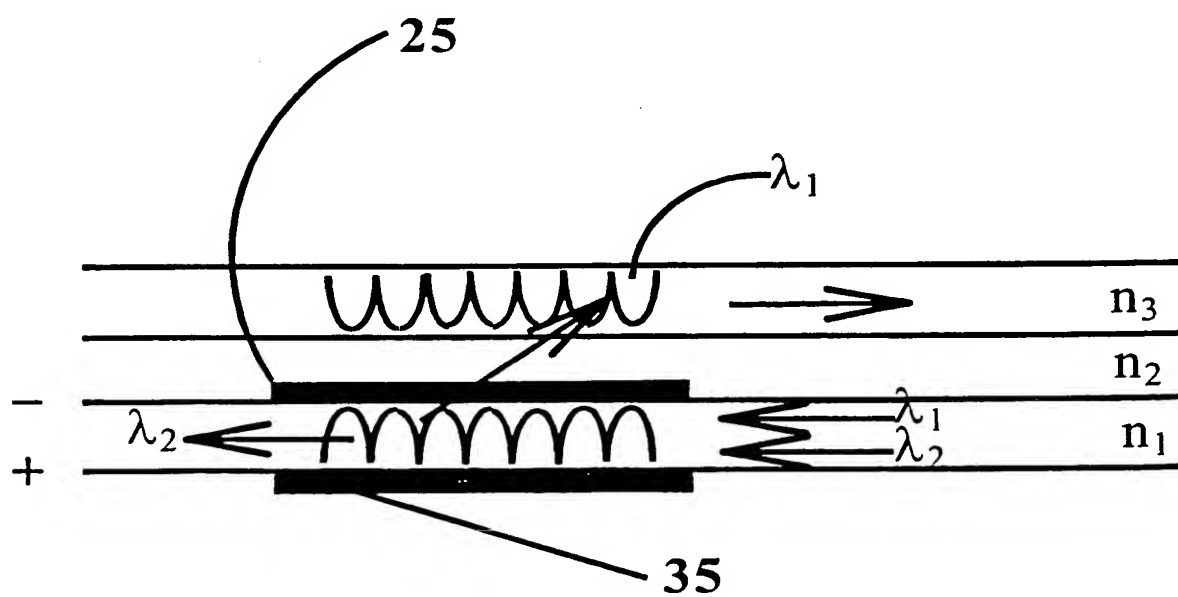


FIGURE 15

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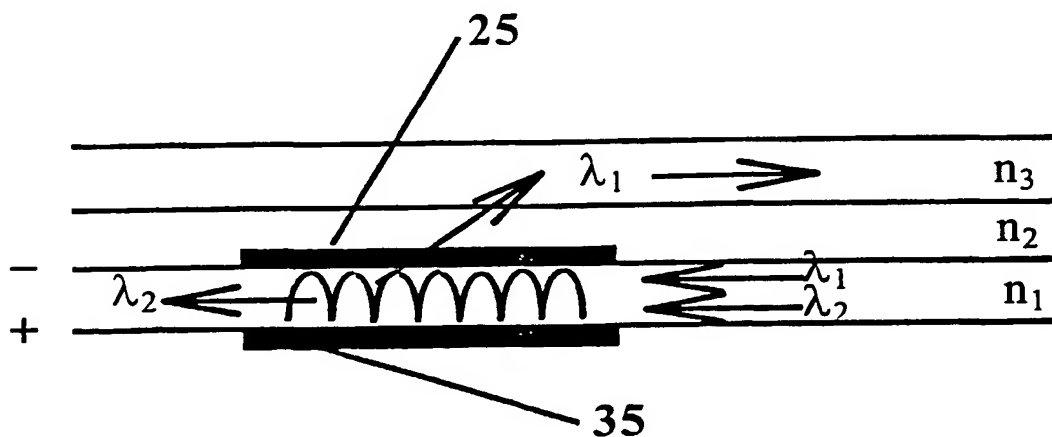
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*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: A MULTI-FUNCTIONAL OPTICAL SWITCH AND ITS METHOD OF MANUFACTURE



(57) Abstract: The invention provides a multifunctional optical switch that among other things, optionally can function as an optical wavelength division multiplexer, wavelength division demultiplexer, add-drop multiplexer and/or inter-connect device. The invention further provides novel methods of manufacturing the optical switch. The optical switch can comprise a single layer, and optimally includes of a plurality of layers which each comprise an optical nonlinear second-order polymer. The optical nonlinear second-order polymer present in each layer differs from that present in any other layer in terms of its absorption maximum (i.e., due to possession of different chromophores).

WO 01/06305 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/19921

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEN T -A ET AL: "TWO-STEP SYNTHESIS OF SIDE-CHAIN POLYIMIDES FOR SECOND-ORDER NONLINEAR OPTICS" MACROMOLECULES,US,AMERICAN CHEMICAL SOCIETY. EASTON, vol. 29, no. 2, 15 January 1996 (1996-01-15), pages 535-539, XP000545164 ISSN: 0024-9297	1
A	the whole document	5-11
Y	--- DONG YU ET AL: "DESIGN AND SYNTHESIS OF FUNCTIONALIZED POLYIMIDES FOR SECOND-ORDER NONLINEAR OPTICS" MACROMOLECULES,US,AMERICAN CHEMICAL SOCIETY. EASTON, vol. 27, no. 23, 7 November 1994 (1994-11-07), pages 6718-6721, XP000476259 ISSN: 0024-9297	1
A	the whole document	5-11,26, 27
Y	--- EP 0 727 692 A (ENICHEM SPA) 21 August 1996 (1996-08-21)	1
A	page 9, line 36 -page 10, line 11	5-11
A	--- US 5 659 010 A (YOSHIMURA TETSUZO ET AL) 19 August 1997 (1997-08-19)	1-3,5,7, 10-12, 18,20, 24,25,29
	figures 7,8; examples 1,3	
A	--- WATARU SOTOYAMA ET AL: "DIRECTIONAL-COUPLED OPTICAL SWITCH BETWEEN STACKED WAVEGUIDE LAYERS USING ELECTRO-OPTIC POLYMER" JAPANESE JOURNAL OF APPLIED PHYSICS,JP,PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, vol. 31, no. 8B, 15 August 1992 (1992-08-15), pages L1180-L1181, XP000355428 ISSN: 0021-4922	2,3,12, 18,20,24
	the whole document	
A	--- EP 0 617 314 A (FUJITSU LTD) 28 September 1994 (1994-09-28)	2-4,7, 12,14, 16,18, 24,28,30
	figures 13,21-26; examples 10,16,21	
	--- -/--	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/19921

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19921

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0727692 A	21-08-1996	US 5736592 A	07-04-1998
		AU 703872 B	01-04-1999
		AU 4336496 A	29-08-1996
		JP 8269326 A	15-10-1996
		KR 199865 B	15-06-1999
		SG 35504 A	01-02-1997
US 5659010 A	19-08-1997	JP 6175172 A	24-06-1994
		US 5459232 A	17-10-1995
		US 5612449 A	18-03-1997
		US 5594093 A	14-01-1997
EP 0617314 A	28-09-1994	US 5757989 A	26-05-1998
		WO 9406052 A	17-03-1994
		US 6215585 B	10-04-2001
EP 0778479 A	11-06-1997	JP 9218316 A	19-08-1997
		US 5859941 A	12-01-1999

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